REACTIONS OF RADICALS CONTAINING FLUORINE

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by

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CONTENTS

PREFACE

The research described in this thesis was carried out by the author in the Department of Chemistry of the University of Edinburgh, under the supervision of Dr. J.C.J. Thynne, between October 1966 and October 1969, is claimed as original, and has not been submitted for a degree elsewhere; with the following exceptions.

a) Methyl radical attack on trifluoroacetaldehyde was investigated in partial fulfilment of the requirements for the degree of B.Sc., with honours in chemistry, in this University.

b) Much of the experimental work on methyl radical attack on perfluoropropionaldehyde and perfluorobutyraldehyde was carried out by Mr. N.C. Beaton, the author having been responsible for the construction and maintenance of the apparatus, preparation of the aldehydes, and partial supervision of the research project.

Department of Chemistry,
University of Edinburgh. 1st October 1969.

DEDICATION

To my Mother.

ACKNOWLEDGEMENTS

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ABSTRACT

The following Arrhenius parameters for hydrogen (or deuterium) atom abstraction have been measured.

Substrate	Radical	Source	Temp. Range (°K)	Log A	E
(CH_3OH)	$CF_3\cdot$	TFMI	357-435	9·92±·15	3·74±·27
$CD_3O\underline{H}$	"	"	" "	9·48±·35	3·24±·63
$C\underline{D}_3OH$	"	"	" "	10·20±·23	6·61±·63
$C\underline{H}_3OH$	"	"	" "	10·0	4·7
$(n\text{-}C_4H_{10})$	$CF_3\cdot$	TFMI	357-435	11·31±·16	5·74±·28
$(n\text{-}C_4H_{10})$	"	HFA	" "	11·77±·24	6·19±·43
$(cyclo\text{-}C_6H_{12})$	"	TFMI	" "	12·16±·16	6·39±·28
$(cyclo\text{-}C_6H_{12})$	"	HFA	" "	12·5	6·2
(CH_3NH_2)	$CF_3\cdot$	TFMI	303-435	10·79±·16	4·19±·26
$CD_3N\underline{H}_2$	"	"	" "	9·94±·22	4·39±·37
$C\underline{D}_3NH_2$	"	"	" "	11·03±·09	6·05±·16
$C\underline{H}_3NH_2$	"	"	" "	10·7	4·2
$((CH_3)_2NH)$	$CF_3\cdot$	TFMI	303-370	11·48±·12	4·14±·18
$(C\underline{H}_3)_2ND$	"	"	323-370	11·85±·51	5·06±·82
$(CH_3)_2N\underline{D}$	"	"	" "	10·91±·29	4·71±·46
$(CH_3)_2N\underline{H}$	"	"	" "	10·5	3·3
$(CH_3)_3N$	$CF_3\cdot$	TFMI	303-435	11·85±·12	4·46±·19
$((CH_2)_2NH)$	"	"	" "	11·03±·17	4·14±·27
CF_3CHO	$CF_3\cdot$	HFA	435-556	11·96±·10	8·78±·22
C_2F_5CHO	"	"	357-556	11·12±·09	6·70±·20
$n\text{-}C_3F_7CHO$	"	"	400-556	11·09±·11	6·57±·22
CF_3CHO	$CH_3\cdot$	DTBP	401-445	12·10±·16	8·7±·3
C_2F_5CHO	"	"	398-438	12·93±·21	9·8±·3
$n\text{-}C_3F_7CHO$	"	"	" "	13·19±·18	10·3±·4

Substrate	Radical	Source	Temp.Range (°K)	Log A	E
SiH_4	$CH_3\cdot$	AZO	323-476	11·82±·09	6·89±·16
"	$CF_3\cdot$	TFMI	313-400	11·90±·25	5·11±·39
$(CH_3)_4Si$	$CH_3\cdot$	AZO	370-526	11·53±·20	10·30±·40
"	$CF_3\cdot$	TFMI	345-526	12·00±·10	7·61±·18
$((CH_3)_3SiH)$	$CH_3\cdot$	AZO	345-526	11·42±·10	7·92±·18
"	$CF_3\cdot$	TFMI	323-476	12·32±·09	5·64±·15
$(CH_3)_3S\underline{i}H$	$CH_3\cdot$	AZO	345-526	11·3	7·8
"	$CF_3\cdot$	TFMI	323-476	12·3	5·5

E is in kcal/mole, A in $mole^{-1}cm^3sec^{-1}$

In cases of ambiguity, the hydrogen or deuterium atom abstracted is underlined. Where the substrate is in brackets, the Arrhenius parameters refer to overall abstraction. (Error Limits ± 1 Standard Deviation)

TFMI ~ trifluoromethyl iodide HFA ~ hexafluoroacetone

DTBP ~ di-tertiary-butyl peroxide AZO ~ azomethane

A value of 1·95 ± ·07, which is independent of temperature, has been obtained for the cross-combination ratio of the radicals $CF_3\cdot$ and $C_2F_5\cdot$.

Butene formed during the photolysis of HFA in the presence of n-butane is attributed to the disproportionation reaction

$$C_4H_9\cdot + CF_3\cdot \longrightarrow C_4H_8 + CF_3H$$

Similar reactions of other alkyl and perfluoroalkyl radicals are discussed. Inhibition of olefin formation (and consequently of formation of fluoroform other than by abstraction)

when TFMI is used as radical source, is explained in terms of the removal of alkyl radicals by reactions of the type

$$R\cdot + I \longrightarrow RI$$

$$R\cdot + I_2 \longrightarrow RI + I\cdot$$

The importance of the reaction

$$R_fCHO + h\nu \longrightarrow R_fH + CO$$

in the photolysis of perfluoroaldehydes is discussed, and has been shown by photolysing R_fCHO in the presence of nitric oxide.

The formation of perfluoroethane and fluoroform during the photolysis of TFMI/Ammonia mixtures cannot be explained solely by the reactions

$$CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6$$

$$\text{and} \quad CF_3\cdot + NH_3 \longrightarrow CF_3H + NH_2\cdot$$

Rate constants for $CF_3\cdot$ attack on polar molecules are interpreted in terms of dipole-dipole interactions between the radical and the substrate molecule. Activation energies measured for hydrogen atom abstraction by $CF_3\cdot$ were found to fall below those for $CH_3\cdot$ by amounts close to 3 kcal/mole.

CHAPTER 1

Substitution of atoms of fluorine for those of hydrogen may have profound effects on the physical and chemical behaviour of a substance. In the last thirty years considerable industrial and scientific interest has been aroused by the electrical properties and chemical inertia of materials such as PTFE. Fluorocarbon analogues of most of the homologous series of organic compounds have been prepared, and the study of their reactions represents a major area of chemical research. The object of the present work is to extend our knowledge of the reactions of perfluoroalkyl radicals, and to compare their behaviour with that of alkyl radicals. Where the necessary data for comparison have not been reported the corresponding alkyl radical reactions have also been studied.

Reactions of free radicals occur in such a way as to reduce the instability generally associated with their possession of an unpaired electron. The principal modes of reaction are outlined below.

COMBINATION:

$$R\cdot + R\cdot' \longrightarrow RR'$$

The rate of such a reaction is governed by two factors: the third-body requirement which, at pressures above a few cm., is significant only for combination of atoms, and steric effects, most marked in the case of complex radicals.

DISPROPORTIONATION:

e.g. $C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_2H_6 + C_2H_4$

The activation energies for both combination and disproportionation reactions are generally taken to be zero, although some workers have reported slight positive values. It follows that the disproportionation/combination ratio is independent of temperature. (e.g. For ethyl radicals the rate of formation of ethylene, $R_{C_2H_4} = 0{\cdot}13\ R_{C_4H_{10}}$.)

ADDITION:

$$R\cdot + A = B \longrightarrow RAB\cdot$$

Free radicals will readily add to an unsaturated molecule to form a larger radical.

DECOMPOSITION:

$$RAB\cdot \longrightarrow R\cdot + A = B$$

Radicals can decompose to produce an unsaturated molecule and a smaller radical.

ISOMERISATION:

The stability of many of the larger free radicals may be increased by the migration of atoms or groups of atoms.

e.g. $CH_3CH_2CH_2CH_2\dot{C}H_2 \longrightarrow CH_3CH_2CH_2\dot{C}H\ CH_3$ (1)

TRANSFER REACTIONS:

$$R\cdot + R'X \longrightarrow RX + R'$$

a) DISPLACEMENT: Here the radical R· takes the place of an atom or group in a molecule.

b) ABSTRACTION: The species abstracted, X, may be an atom or group. The distinction between group displacement and group abstraction is not clear-cut, but depends

on the relative sizes of R' and X. e.g. The reaction

$$CF_3\cdot + CD_3OH \longrightarrow CF_3OH + CD_3\cdot$$

encountered in this work, could be regarded as abstraction of a hydroxyl group, or displacement of a trideuteromethyl group, by a trifluoromethyl radical.

While no investigation of isomerisation or decomposition of organo-fluorine radicals has been described, the other modes of reaction mentioned above have been the subject of a considerable amount of research, which is summarised after the following brief discussion of available radical sources.

RADICAL SOURCES

Trifluoromethyl radicals may be generated by photolysis of such molecules as hexafluoroacetone (HFA), hexafluoroazomethane (HFAM), trifluoromethyl iodide (TFMI) or trifluoroacetaldehyde (TFAA). With the exception of the photolysis of acetone itself, few other photodecompositions have been studied so extensively as that of hexafluoroacetone. (7,8) It is possible that both modes of decomposition shown below occur, although no thermochemical evidence is available to substantiate or disprove this.

$$CF_3COCF_3 + h\nu \longrightarrow CF_3CO\cdot + CF_3\cdot$$

$$CF_3COCF_3 + h\nu \longrightarrow 2CF_3\cdot + CO$$

In view of the carbon-fluorine bond strength, however, (4) the decomposition:

$$CF_3COCF_3 + h\nu \longrightarrow CF_3COCF_2\cdot + F\cdot$$

may safely be discounted.

HFA and HFAM have the advantage that the amount of carbon-monoxide or nitrogen formed provides a measure of the overall quantum yield. In both cases, however, $CF_3\cdot$ radicals may be lost by addition to the parent molecule. This is a serious disadvantage when a material balance method is to be employed.

$$CF_3N = NCF_3 + CF_3\cdot \longrightarrow \begin{matrix} CF_3 \\ \diagdown \\ \quad N\text{-}\dot{N}\text{-}CF_3 \\ \diagup \\ CF_3 \end{matrix}$$

$$\begin{matrix} CF_3 \\ \diagdown \\ \quad C = O \\ \diagup \\ CF_3 \end{matrix} + CF_3\cdot \rightleftharpoons \begin{matrix} CF_3 \\ \diagdown \\ \quad C \\ \diagup \\ CF_3 \end{matrix}\!\!\begin{matrix} CF_3 \\ \diagup \\ \quad O\cdot \end{matrix} \xrightarrow{CF_3\cdot} \begin{matrix} CF_3 \\ | \\ CF_3\text{-}C\text{-}O\text{-}CF_3 \\ | \\ CF_3 \end{matrix} \qquad (10)$$

The reversability of addition to the carbonyl group was demonstrated by Alcock and Whittle (11) who observed trifluoroacetone amongst the products from photolysis of HFA/CH_3I mixtures.

The photolysis of acetone or azomethane is widely used for the generation of methyl radicals. In both cases abstraction of hydrogen from the parent molecule is an important mode of reaction for the radicals formed.

$$CH_3COCH_3 + CH_3\cdot \longrightarrow CH_4 + CH_3COCH_2\cdot$$

$$CH_3N_2CH_3 + CH_3\cdot \longrightarrow CH_4 + CH_3N_2CH_2\cdot$$

Where the rate of formation of methane is used as an index of the rate of a reaction under study in the system, a correction must be made to allow for this. In some cases this may account for most of the methane formed, leading to

the possibility of serious accumulation of error in the desired rate constant. This difficulty is encountered with all sources of alkyl radicals. $CF_3\cdot$ radicals, however, will not abstract fluorine from trifluoromethyl groups (7,8,10), leading to much simpler systems. The photolysis of perfluorodiethyl ketone has been used as a source of $C_2F_5\cdot$ radicals (13) and again no abstraction of fluorine from the parent compound is observed. Similarly perfluorodi-n-propyl ketone represents a clean source of $C_3F_7\cdot$ radicals. (18)

$$C_3F_7COC_3F_7 + h\nu \longrightarrow 2C_3F_7\cdot + CO$$

This split (Norrish type I) is the only mode of decomposition observed. No Norrish type II split

$$C_3F_7COC_3F_7 + h\nu \longrightarrow CF_3COC_3F_7 + C_2F_4$$

has been reported.

Photolysis of trifluoroacetone yields CO, CH_4, C_2H_6, CF_3CH_3 and C_2F_6, with again no formation of CF_4 or CH_3F. Sieger and Calvert, who first studied this radical source, (19) proposed the following split as the major primary photolytic process:

$$CF_3COCH_3 + h\nu \longrightarrow CF_3CO\cdot + CH_3\cdot$$

This is unlikely to be the case, however, since there is no evidence of the formation of products resulting from the trifluoroacetyl radical. In a more recent investigation (20) biacetyl was identified among the reaction products, suggesting that the principal mode of decomposition is:

$$CH_3COCF_3 + h\nu \longrightarrow CH_3CO\cdot + CF_3\cdot$$

The yields of methane and ethane, however, indicate that

$$CH_3COCF_3 + h\nu \longrightarrow CH_3\cdot + CF_3\cdot + CO$$

may also occur to a significant extent.

Photolysis of TFMI (14) forms a convenient source of trifluoromethyl radicals, free from addition reactions with the parent molecule. The presence of iodine atoms in the system conveniently inhibits secondary reactions. This is discussed more fully in Chapter 3. Perfluoroethyl-iodide has also been used as a photolytic radical source (14).

Photolysis of perfluoroaldehydes would appear to provide a further useful source of fluorinated alkyl radicals, and is a widely used method of obtaining $C_2F_5\cdot$ and $C_3F_7\cdot$ (15,16,17). The principal reactions are normally taken to be:

1) $R_fCHO + h\nu \longrightarrow R_f\cdot + CHO\cdot$

2) $R_f\cdot + R_fCHO \longrightarrow R_fH + R_fCO\cdot$

3) $R_f\cdot + R_f\cdot \longrightarrow R_{f_2}$

Dodd and Smith (17) photolysed trifluoroacetaldehyde and obtained an activation energy of 8·4 k·cal/mole for reaction 2. Later investigation of the photolysis of C_2F_5CHO and C_3F_7CHO by G.O. Pritchard and his co-workers (15) gave values of 4·5 and 4·0 k.cal/mole respectively for the activation energy, and they concluded that Dodd and Smith's result was "improbably high". One of the aims of the present work was to attempt to resolve this discrepancy, and it now appears that the reaction:

$$R_fCHO + h\nu \longrightarrow R_fH + CO$$

represents an important mode of decomposition. This is discussed fully in Chapter 7.

Alkyl radicals may similarly be produced by the photolysis of ketones, iodides, aldehydes and azo-compounds. There also exist a number of sources which are not yet available for generation of fluorinated radicals. These include the thermal decomposition of metal alkyls (dimethyl mercury, tetramethyl lead, etc.), (21,22,23), pyrolysis of alkyl nitrites, (24)

$$RCH_2ONO \longrightarrow RCH_2O\cdot + NO$$
$$\downarrow$$
$$R\cdot + HCHO$$

and the mercury photosensitised decomposition of alkanes (25).

$$\text{e.g. } C_2H_6 + Hg\,6^3P_1 \longrightarrow C_2H_6^* + Hg\,6^1S_o$$
$$\downarrow$$
$$C_2H_5\cdot + H\cdot$$

Di-tertiary-butyl peroxide is a useful source of methyl radicals (26) due to the instability of the t-butoxyl radical formed initially on thermal decomposition.

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + CH_3COCH_3$$

Diacetyl peroxide decomposes to give two acyloxy radicals which then further decompose to carbon dioxide and methyl radicals.

$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \longrightarrow 2CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\cdot$$

$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\cdot \longrightarrow CH_3\cdot + CO_2$$

Chapter 3 includes a description of an unsuccessful attempt to extend the use of acyloxyl radicals as alkyl radical precursors by the use of dimethylazodiformate as a radical source. It was thought that the following thermal decomposition might occur, with the formation of nitrogen and carbon dioxide providing a measure of the rate of formation of methyl radicals.

$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}N = N\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \longrightarrow 2CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\cdot + N_2$$

$$\downarrow$$

$$2CH_3\cdot + 2CO_2$$

Unfortunately this simple reaction scheme is not obeyed.

COMBINATION OF FREE RADICALS

The absolute rate constant for combination, k_c, has been measured for a number of radicals. The method most commonly used is the rotating sector technique which has been fully described by Melville and Burnett (31). Essentially, the mean lifetime of radicals generated photolytically is determined using intermittent illumination, and hence, knowing the rate of release of radicals into the system, their concentration, and hence k_c, may

be determined. Using this method absolute rate constants for recombination of $CH_3\cdot$ and $CF_3\cdot$ radicals have been measured.

METHYL: $\text{Log}_{10}\, k_c = 13{\cdot}34$ (28,32,33)

TRIFLUOROMETHYL: $\text{Log}_{10}\, k_c = 13{\cdot}36$ (35)

(k_c is in mole^{-1} cm.^3 sec.^{-1})

Although there is some evidence (36) to suggest that these reactions may have a slight temperature dependence, no reliable values exist for the activation energies. It is well established, however, that these are extremely small, if not zero, (11,35,37,38) and, in accordance with current kinetic practice, the above rate constants are therefore assumed to be independent of temperature.

It is well established, however, that k_c is pressure dependent. Combination of two radicals produces a "hot" molecule which, of course, possesses sufficient energy for decomposition.

$$R\cdot + R\cdot \rightleftharpoons R_2^* \xrightarrow{M} R_2$$

The lifetime of such a species is dependent on the number of vibrational degrees of freedom into which this energy may be dissipated. Thus the probability of stabilisation by collision rather than redissociation increases with the complexity of the radicals involved, (28,29,30). For methyl and trifluoromethyl radicals decomposition becomes negligible at pressures greater than about 10 torr.

The recombination of methyl radicals has been studied

by a number of other methods including direct sampling from a flow system into the chamber of a mass-spectrometer (39,40) measurement, using a sensitive diaphragm manometer of pressure changes resulting from the adiabatic temperature change which occurs during the photolysis of acetone (41,42) and pulsed photolysis, an intermittent illumination technique in which the period of illumination is shorter than in the rotating sector method by a factor of about 1000 (43). Results obtained substantiate the value of k_c quoted above. These methods have not been applied to the combination of $CF_3\cdot$ radicals, however, and no absolute rate constants have been reported for the combination of higher perfluoroalkyl radicals.

As well as auto-combination reactions of this type, cross-combination can occur between two different radicals.

$$A\cdot + A\cdot \longrightarrow A_2 \qquad (k_{aa})$$

$$A\cdot + B\cdot \longrightarrow AB \qquad (k_{ab})$$

$$B\cdot + B\cdot \longrightarrow B_2 \qquad (k_{bb})$$

According to the simple collision theory of chemical kinetics, the cross-combination ratio

$$\Phi = \frac{k_{ab}}{k_{aa}^{\frac{1}{2}} \cdot k_{bb}^{\frac{1}{2}}}$$

should equal 2 for reactions of zero activation energy. If we denote the rate of formation of A_2 by R_{a_2}, etc., then it follows that:

$$\Phi = \frac{R_{ab}}{R_{a_2}^{\frac{1}{2}} R_{b_2}^{\frac{1}{2}}}$$

For small alkyl and perfluoroalkyl radicals, cross-combination ratios close to 2 are in fact found, often over a considerable temperature range. (52,93)

From a study of the photolysis of mixtures of acetone and hexafluoroacetone Pritchard and Dacey reported a high, temperature-dependent value for the cross-combination ratio of methyl and trifluoromethyl radicals, which they explained by assigning an activation energy of about 2 kcal./mole to the recombination of $CF_3\cdot$. A later study of this system by Giles and Whittle (38) revealed the formation of appreciable quantities of $CH_2 = CF_2$. This is explained by the following reaction scheme.

$$CH_3\cdot + CH_3\cdot \rightleftharpoons CH_3CF_3^* \xrightarrow{k_e} CH_2 = CF_2 + HF$$

$$CH_3CF_3^* \xrightarrow{M,\ k_s} CH_3CF_3$$

Thus the "hot" trifluoroethane molecule formed initially may be deactivated by collision, or may react by elimination of HF. If the cross-combination ratio is calculated using the combined rate of formation of CH_3CF_3 and $CH_2 = CF_2$ then, within experimental error, a value of 2 is obtained, which is independent of temperature. Elimination of hydrogen fluoride from activated fluoroethanes was first observed during the photolysis of 1,3-difluoroacetone (44). Similar reactions have been observed for the initial products of

combination of the following pairs of radicals.

$CH_3\cdot + CH_2F\cdot$; $CH_2F\cdot + CF_2H\cdot$; $CF_2H\cdot + CF_2H\cdot$;

$CH_3\cdot + CF_2H\cdot$; $CH_3\cdot + CH_3CF_2\cdot$; $CH_3\cdot + CF_2HCH_2\cdot$ (45,46,47)

The Rice-Ramsperger-Kassel theory of unimolecular reactions has been used to calculate values of k_s/k_e for the various energised ethanes formed by combination of these radicals (46,48), leading to the conclusion that the probability of HF elimination decreases as the number of fluorine atoms in the molecule increases, the value of k_s/k_e for C_2HF_5 being about 2000 times greater than that for C_2H_5F. Quantitative predictions from this theory are in good agreement with experimental results. In particular Giles, Quick and Whittle, (49) who investigated the combination of $CF_3\cdot$ and $CF_2H\cdot$, detected no perfluoroethylene among the products, showing that, as predicted, elimination is not, in fact, an important mode of reaction of the activated C_2HF_5 molecule. No elimination of HF is reported for the following radical pairs. (16,50,51)

$CH_3\cdot + C_3F_7\cdot$; $C_2H_5\cdot + C_3F_7\cdot$; and $C_2H_5\cdot + C_2F_5\cdot$

It has been suggested (51) that the molecules formed on combination may possess enough vibrational degrees of freedom to dissipate the excess energy internally.

Ratios obtained for the cross-combination of alkyl radicals with perfluoroalkyls are commonly high, or temperature dependent (16,50,51,53). This has been attributed to polar effects (16), but in view of Whittle's

value for the cross-combination ratio of $CF_3\cdot$ and $CH_3\cdot$ this explanation seems unsatisfactory. Results obtained in the course of the present work suggest that, for reactions involving ethyl or higher alkyl radicals, these anomalous values may be explained in terms of an alternative route to the cross-combination product, while re-examination of the published data for combination of $CH_3\cdot$ and $C_3F_7\cdot$ casts grave doubts on the validity of the conclusions reached. This is discussed more fully in Chapter 8.

DISPROPORTIONATION REACTIONS

Although the strength of the carbon-fluorine bond precludes the occurrence of reactions such as:

$$C_2F_5\cdot + C_2F_5\cdot \longrightarrow CF_2 = CF_2 + C_2F_6$$

cross-disproportionation reactions between alkyl and perfluoroalkyl radicals occur readily.

e.g. $C_2H_5\cdot + C_2F_5\cdot \longrightarrow CH_2 = CH_2 + C_2F_5H$

As mentioned above, however, an alternative route to the cross-combination product is thought to exist, which would invalidate published disproportionation/combination ratios for such reactions.

Partially fluorinated methyl radicals may undergo a type of disproportionation reaction in which a bi-radical is formed.

e.g. $CF_2H\cdot + CF_2H\cdot \longrightarrow CF_2: + CF_2H_2$ (45,55,56)

while HF elimination, discussed above, may be regarded as

a disproportionation reaction.

e.g. $CFH_2 + CFH_2 \longrightarrow CFH = CH_2 + HF$ (44)

ADDITION REACTIONS

The initial product from addition of a free radical to an unsaturated molecule is itself a radical.

$R\cdot + A = B \longrightarrow RAB\cdot$

This may then react by abstraction, either from the radical source or from A = B, by a further addition step (which could give rise to a head-to-head or head-to-tail linkage), or by disproportionation or combination with another radical, $R\cdot$ or $R(AB)_n\cdot$. This leads to a large number of products of widely differing molecular weights, making complete product analysis impracticable.

In order to circumvent this difficulty Szwarc and his co-workers adopted a material balance method. HFAM was photolysed in the presence of 2,3-dimethylbutane, and the ratio $(CF_3H/N_2)_{BLANK}$ measured. The presence of an olefin A = B in the system reduces this ratio due to the competing addition reaction.

$$CF_3N_2CF_3 \longrightarrow 2CF_3\cdot + N_2$$

$$CF_3\cdot + RH \longrightarrow CF_3H + R\cdot \quad (k_a)$$

$$CF_3\cdot + A = B \longrightarrow CF_3AB\cdot \quad (k_b)$$

$$(RH \equiv CH_3-\overset{H}{\overset{|}{C}}(CH_3)-\overset{H}{\overset{|}{C}}(CH_3)-CH_3)$$

Taking these as the only reactions involving $CF_3\cdot$ radicals;

$$\frac{k_b}{k_a} = \frac{[RH]}{[A = B]} \left\{ \frac{(CF_3H/N_2)_{BLANK}}{(CF_3H/N_2)_{OLEFIN}} - 1 \right\}$$

It is evident, however, that other reactions are possible, including abstraction from the olefin (allylic hydrogens being particularly labile), and radical-radical reactions such as

$$CF_3AB\cdot + CF_3\cdot \longrightarrow CF_3ABCF_3 .$$

Using this method Szwarc studied the addition of trifluoromethyl radicals to a large number of unsaturated substances, obtaining values for $E_a - E_b$ and A_b/A_a. (57,58,59) When this work was carried out the only reported value for E_a was 1·7 k.cal/mole (60) leading to negative values of E_b for most of the systems studied. A recent re-investigation of the abstraction of hydrogen from 2,3-dimethylbutane by trifluoromethyl radicals has yielded a value of 3·3 k.cal/mole for E_a which is entirely compatible with the accepted value for abstraction by methyl radicals. Use of this more reliable activation energy leads to positive values of E_b in most cases, but not all. It therefore appears that $CF_3\cdot$ reactions neglected in this treatment lead to appreciable errors in the ratio k_b/k_a. This is borne out by a recent investigation (61) of the photolysis of TFMI/ethylene mixtures in the presence of a large excess of hydrogen sulphide. The hydrogen atoms in H_2S are extremely labile, making abstraction the preferred mode of reaction of the $CF_3AB\cdot$ radical. Thus the formation of products of high molecular weight is inhibited, making complete product analysis possible. This direct method gives the following Arrhenius parameters for the reaction

$$CF_3\cdot + CH_2 = CH_2 \longrightarrow CF_3CH_2CH_2\cdot$$

$E = 2\cdot4$ k.cal/mole. $\log_{10}A = 11\cdot4$ (mole^{-1}cm.^{3}sec.$^{-1}$)

By comparison Swarc obtained:

$E = 1\cdot0$ k.cal/mole. $\log_{10}A = 11\cdot0$

The corresponding parameters for addition of methyl radicals to ethylene are: (94)

$E = 6\cdot8$ k.cal/mole. $\log_{10}A = 11\cdot1$

Thus at room temperature the rate of addition of $CF_3\cdot$ radicals to ethylene is about four thousand times that for $CH_3\cdot$. This is likely to be due mainly to dipole/induced-dipole attraction between the readily polarised olefin molecule and the highly polar attacking radical.

Whittle and his co-workers have investigated the addition of trifluoromethyl radicals to benzene and a large number of its substituted alkyl and halogen derivatives (62,63,64), using a material balance method based on the following reactions.

$$CF_3COCF_3 + h\nu \longrightarrow 2CF_3\cdot + CO$$

$$CF_3\cdot + C_6H_6 \longrightarrow CF_3H + C_6H_5\cdot \quad (k_a)$$

$$CF_3\cdot + C_6H_6 \longrightarrow CF_3C_6H_6\cdot \quad (k_b)$$

$$CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6 \quad (k_c)$$

Neglecting the reaction $CF_3C_6H_6\cdot + CF_3\cdot \longrightarrow CF_3C_6H_6CF_3$,

$$k_b = k_c^{\frac{1}{2}} \frac{2R_{CO} - R_{CF_3H} - 2R_{C_2F_6}}{R_{C_2F_6}^{\frac{1}{2}} [C_6H_6]}$$

Trifluoromethyl radicals will also add to carbonyl and azo groups, as outlined previously in the discussion of radical sources. No reliable kinetic data exist for addition reactions of higher perfluoroalkyl radicals.

ABSTRACTION REACTIONS

Halogen atom abstraction from carbon tetrachloride, chloroform, dichloromethane, methylchloride, methylbromide and methyliodide by CF_3 radicals has been studied by Alcock and Whittle. (11,65) Arrhenius parameters have also been reported (64) for abstraction of halogen atoms from halobenzenes and toluenes by trifluoromethyl radicals. It is thought, however, that this is preceded by an addition reaction, with abstraction taking place from the addition complex.

i.e. $CF_3\cdot + ArX \longrightarrow CF_3ArX$

$CF_3\cdot + CF_3ArX \longrightarrow CF_3X + ArCF_3$

In all cases abstraction of chlorine was found to be an extremely difficult process, while as previously mentioned, no abstraction of fluorine has been observed.

Most research on transfer reactions of trifluoromethyl radicals, however, has dealt with hydrogen atom abstraction. If the reactions;

$CF_3\cdot + RH \longrightarrow CF_3H + R\cdot$ (k_a)

and $CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6$ (k_c)

are, respectively, the only source of fluoroform and hexafluoroethane, then we may define:

$$R = \frac{k_a}{k_c^{\frac{1}{2}}} = \frac{R_{CF_3H}}{R_{C_2H_6}^{\frac{1}{2}}[RH]}$$

As mentioned in the section on radical combination reactions:

$$k_c = 10^{13\cdot36} \text{ mole}^{-1}\text{cm}^3\text{sec}^{-1}$$

$$\therefore \log_{10} k_a = 6\cdot68 + \log_{10} R$$

Now, expressing k_a in terms of the simple Arrhenius equation $k = A\exp(-E/RT)$

$$\log_{10} k_a = \log_{10} A - (E/2\cdot303RT)$$

$$\log_{10} R = (\log_{10} A - 6\cdot68) - (E/4\cdot576T)$$

Thus a plot of $\log_{10} R$ against 1,000/T, where T is the absolute temperature, has intercept $(\log_{10} A - 6\cdot68)$ and gradient $E/4\cdot576$ where E is the activation energy for abstraction in k.cal/mole.

When the present work commenced (1966), a considerable amount of kinetic data had been obtained for abstraction by $CF_3\cdot$ from hydrocarbons, and Arrhenius parameters had also been reported for abstraction from acetone, acetaldehyde, trifluoroacetone and trifluoroacetaldehyde (68). Whittle had also investigated the abstraction of hydrogen from a number of partially halogenated methane derivatives (11,12,66). With the exception of Arthur and Bell's work on hydrogen sulphide, (69) and a study by Carlton et al. (70) of abstraction from methanol and its deuterated derivatives, all available kinetic data referred to reactions in which only carbon - hydrogen bonds were severed. For this

reason reactions of $CF_3\cdot$ with molecules containing OH, SH, NH and SiH as well as CH linkages were investigated. By studying polar molecules it has also been possible to observe the effects of dipole interactions with the strongly polar fluoroalkyl radicals. Since hydrocarbon molecules are virtually non-polar, little was known of the way in which such interactions affect Arrhenius parameters for hydrogen abstraction.

Considerably less work has been done on transfer reactions of higher perfluoroalkyl radicals. The reactions

$$R_f\cdot + H_2 \longrightarrow R_fH + H\cdot \qquad \text{and}$$

$$R_f\cdot + D_2 \longrightarrow R_fD + D\cdot$$

have been studied for $R_f = CF_3$, C_2F_5, and $n\text{-}C_3F_7$. The extent to which reactions of the type

$$R_f\cdot + H\cdot \longrightarrow R_fH$$

contribute to the R_fH yield is not known, however, making these results subject to considerable uncertainty. Arrhenius parameters have also been reported for the reaction of $C_2F_5\cdot$ with methane (13), and $n\text{-}C_3F_7\cdot$ with methane, ethane, cyclohexane and acetone. (16,53,74,76) Reactions of the type:

$$R_f\cdot + R_fCHO \longrightarrow R_fH + R_fCO\cdot$$

have already been dealt with in the discussion of radical sources.

An important unifying conclusion which emerged from the extensive study of abstraction from hydrocarbons by

$CF_3\cdot$ radicals is that the activation energy for such reactions is approximately 2·5 k.cal/mole lower than that for the corresponding abstraction by methyl radicals (77). When this work was carried out it was believed that the carbon-hydrogen bond dissociation energy for fluoroform, $D(CF_3\text{-}H)$, was approximately 103 k.cal/mole, only slightly greater than $D(CH_3\text{-}H)$, and an explanation of this activation energy difference based on the high polarity of the $CF_3\cdot$ radical was proposed (60). Later work by Whittle and his colleagues, (78), however suggested that a more probable value for $D(CF_3\text{-}H)$ is 105 k.cal/mole. A value of 2·5 k.cal/mole for $D(CF_3\text{-}H) - D(CH_3\text{-}H)$ is now entirely feasible, and it is unnecessary to invoke explanations based on polarity. There is an indication from available evidence that there exists a trend in radical reactivity in the order

$$CF_3\cdot > C_2F_5\cdot > C_3F_7\cdot > CH_3\cdot$$

and that this is paralleled by a decrease in the strength of the carbon-hydrogen bond formed. (13,78) In the absence of sufficient kinetic data, however, this must be regarded as somewhat speculative.

In order to study the relative rates of hydrogen atom abstraction from different sites in the same molecule, deuterium labelling is frequently employed. The activation energy for abstraction of an atom of deuterium, however, is not the same as that for hydrogen. This arises from the fact that in the ground vibrational state a chemical bond possesses a finite vibrational energy known as the zero-point energy. The greater

inertial mass of a deuterium atom leads to a lower zero-point energy than would be associated with a hydrogen atom in the same environment. From this it follows that the activation energy for abstraction of deuterium should be higher than that for the corresponding hydrogen abstraction by the zero-point energy difference, ΔE_o. For a C-H bond ΔE_o is 1·2 k.cal/mole, while for an N-H bond it is 1·3 k.cal/mole (79).

This elementary treatment of the kinetic isotope effect predicts that the pre-exponential Arrhenius parameter should be unaffected.

i.e. $A_H/A_D = 1$

and hence

$$k_H/k_D = e^{-\frac{\Delta E_o}{RT}}$$

Within the limits of experimental error this has been verified for a number of hydrogen and deuterium atom abstractions by methyl and trifluoromethyl radicals. (80-84) It is common practice to assume that secondary isotope effects are negligible, (e.g. to assume that the rate constants for hydrogen atom abstraction from the amino groups in CH_3NH_2 and CD_3NH_2 will be the same). Experimental evidence supports the validity of this assumption (85-89). The way in which kinetic data for abstraction from labelled and unlabelled molecules may be combined is illustrated by the following reactions of methylamine and trideuteromethylamine.

1. $CD_3NH_2 + CF_3\cdot \longrightarrow CF_3D + \cdot CD_2NH_2$
2. $CD_3NH_2 + CF_3\cdot \longrightarrow CF_3H + CD_3NH\cdot$
3. $CH_3NH_2 + CF_3\cdot \longrightarrow CF_3H + \cdot CH_2NH_2$
4. $CH_3NH_2 + CF_3\cdot \longrightarrow CF_3H + CH_3NH\cdot$
5. $CH_3NH_2 + CF_3\cdot \longrightarrow CF_3H + (C_2H_4N)$.

Reaction 5 represents overall abstraction from the undeuterated substrate.

i.e. $k_5 = k_3 + k_4$

But, neglecting secondary isotope effects,

$k_2 = k_4$ therefore $\underline{k_3 = k_5 - k_2}$

The preceding elementary treatment of primary isotope effects predicts that:

$A_2/A_1 = 1$ and $E_1 - E_3 = \Delta E_o = 1{\cdot}2$ k.cal/mole

This simple view of the processes involved, however, is complicated by an effect known as quantum-mechanical tunnelling. Classically, before reaction is possible the system must possess sufficient energy (the activation energy) to reach the activated complex between reactants and products. From a quantum-mechanical standpoint, however, there is a finite probability of reaction for systems of lower energy. This probability is greatest when the De Broglie wavelength of the species involved is comparable with the effective width of the potential barrier. Thus tunnelling is far less likely for deuterium than it is for hydrogen atoms, while the abstraction of larger atoms or groups in this way has not been observed.

Since the relative importance of tunnelling is greatest at low temperatures, the observed activation energy for hydrogen abstraction is likely to be an underestimate of the actual height of the potential energy barrier, possibly by as much as 20%. (68) Since the corresponding lowering will be considerably less in the case of deuterium, the occurrence of the tunnel effect should lead to values of $E_D - E_H$ greater than ΔE_o, and values of A_H/A_D less than unity, as has been observed by a number of workers. (90,91,92)

At present there is no general method which may be used to allow for the effects of tunnelling, and in accordance with general practice Arrhenius parameters obtained in the present work are reported without correction. It is evident, however, that this must be borne in mind when using such parameters for the calculation of bond strengths, or other molecular properties.

For an elementary chemical process the Arrhenius parameters for the reverse reaction (E_r and A_r) may be derived thermochemically from those for the forward reaction. Firstly it is evident that:

$$\underline{E_f - E_r = \Delta H}$$

The equilibrium constant for the reaction, K, is related to the change in free energy by the equation:

$$-RT \ln K = \Delta G = \Delta H - T\Delta S$$

$$\text{But} \quad K = \frac{k_f}{k_r} = \frac{A_f}{A_r} \exp\left(-(E_f - E_r)/RT\right)$$

$$\therefore \quad \ln K = \ln\frac{(A_f)}{(A_r)} - \frac{\Delta H}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\therefore \quad \ln\frac{(A_f)}{(A_r)} = \frac{\Delta S}{R}$$

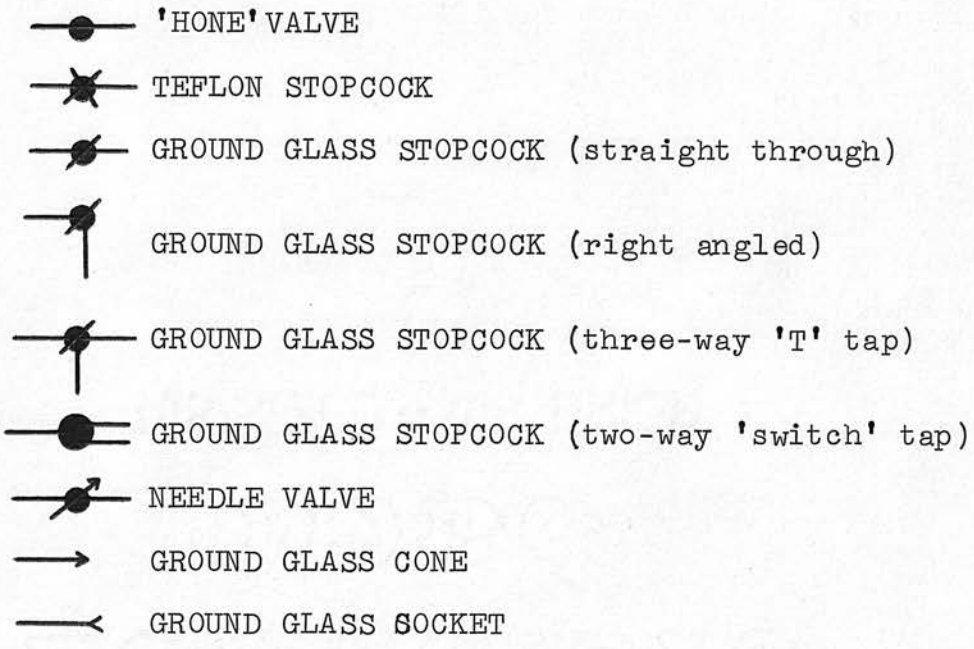
$$\therefore \quad \underline{\log A_r = \log A_f - \Delta S/4{\cdot}576}$$

Using these relationships it has been possible to obtain estimates of Arrhenius parameters for abstraction of hydrogen from fluoroform. Although subject to accumulation of errors from the kinetic and thermochemical values employed, this approach gives access to kinetic data which are frequently unobtainable by direct methods.

CHAPTER 2

1. APPARATUS

The apparatus employed is shown diagrammatically in Fig. 1, using the following symbols:-



A. VACUUM SYSTEM

A pyrex high vacuum system was constructed, the principal components being:

a) THE PUMPING SYSTEM: an EDWARDS "Speedivac" mercury diffusion pump, flanked by two detachable cold traps, and backed by an EDWARDS two stage rotary oil pump.

b) THE STORAGE MANIFOLD: three storage bulbs (with cold-fingers attached) of volume 2 litres, 1 litre, and 500 ml., a vacustat, and two ground-glass cones. All taps on this manifold are ground-glass stopcocks, lubricated with APIEZON-'L' high vacuum hydrocarbon tap grease (A.E.I. Ltd.),

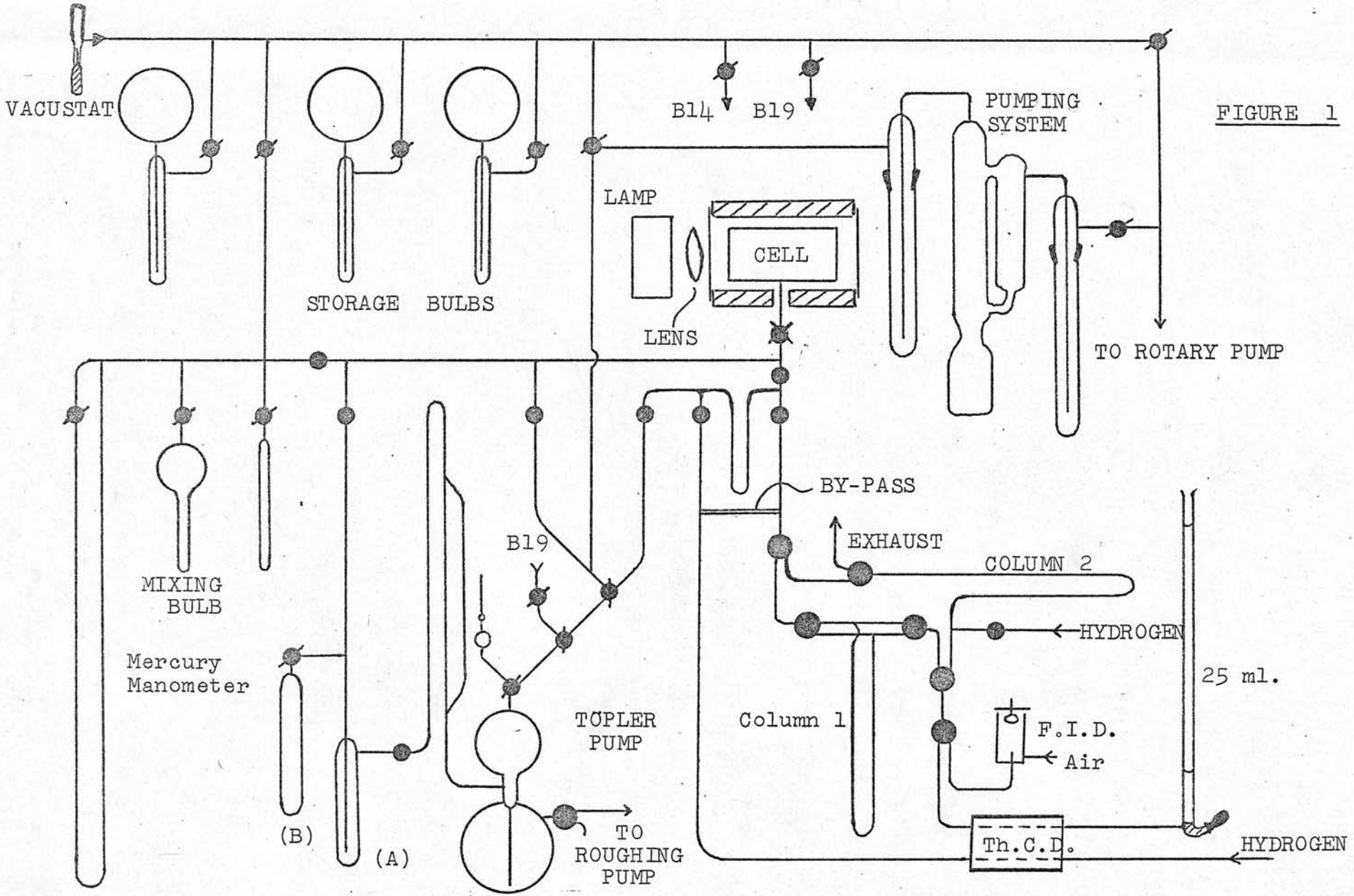

VACUSTAT
STORAGE BULBS
B14
B19
PUMPING SYSTEM
LAMP
CELL
LENS
TO ROTARY PUMP
BY-PASS
EXHAUST
COLUMN 2
HYDROGEN
MIXING BULB
B19
Mercury Manometer
TOPLER PUMP
Column 1
F.I.D.
Air
25 ml.
(B)
(A)
TO ROUGHING PUMP
Th.C.D.
HYDROGEN

FIGURE 1

as is the cone and socket pivot of the vacustat.

c) THE MIXING MANIFOLD: a mercury manometer with mirror scale, a mixing bulb of approximate volume 150 ml., and a small tube for trapping

d) THE CENTRAL MANIFOLD: a low volume manifold, connected by stainless-steel valves with teflon seats (HONE INSTRUMENTS Ltd.) to the mixing manifold, pumping system, cold-trap (A), and chromatography u-tube, and to the reaction cell by a WESTEF teflon stopcock with VITON rubber o-ring seals (WEST-GLASS CORPORATION). The glass-metal seals to the Hone valves were made with ARALDITE epoxy-resin adhesive.

e) GAS MEASUREMENT AND TRANSFER SYSTEM:

A ground-glass stopcock lubricated with KEL-F-90 fluorocarbon high vacuum tap grease (MINNESOTA MINING AND MANUFACTURING Co) joins the cold-trap (A) to a tube (B), which may be used as a sharing volume.

$$\frac{\text{VOLUME OF (A)}}{\text{VOLUME OF (B)}} = 1{\cdot}10 \pm 0{\cdot}01$$

Trap (A) is also connected by a Hone valve to the inlet arm of a Töpler pump. From the bulb of the Töpler pump gases may be driven, through a series of three-way taps, to:-

i) a gas burette

ii) a sample tube attached to a B-14 socket, or

iii) the chromatography u-tube

Using the Töpler pump quantitative transfer may also be effected between any two of these.

The available gas-burette volumes are:-

OA = 0·0722 cc

OB = 0·624 cc

OC = 2·16 cc

where O is the top of the closed limb and A, B, and C are etched marks.

B. GAS CHROMATOGRAPHY SYSTEM

From the cylinder pressure-reduction head the carrier gas (B.O.C. hydrogen or helium) passes through the following

a) a needle valve (EDWARDS)

b) the reference arm of a thermistor thermal conductivity detector (Th.C.D.) GOW-MAC MODEL 9677

c) EITHER the u-tube of the injection system OR a by-pass of glass capillary when the Hone valves to the u-tube are closed

d) EITHER column 1
OR column 2

e) EITHER a flame ionisation detector (F.I.D.)
OR the other arm of the thermal conductivity detector, in which case it then passes through

f) a bubble meter.

All ground-glass stopcocks in this system are spring-loaded to withstand pressures above atmospheric without unseating.

In most runs the measured products were eluted a considerable time before the unchanged reactants, or

products of higher molecular weight. To avoid long waiting periods between runs, the direction of flow through the columns was reversed after the required peaks had appeared.

All columns used consisted of packed loops of 5 mm. O.D. pyrex tubing. The following packings were used:-

SILICA GEL: the 40-60 mesh fraction of B.D.H. silica gel activated by heating under vacuum.

ACTIVATED ALUMINA (100-120 mesh) - Phase Separations Ltd.

DIETHYL ADIPATE ON FIREBRICK: 40-60 mesh fire-brick coated with 20% diethyladipate

The various combinations of column and operating conditions used are summarised in Table 1.

A potential of 270 V was maintained between the collector plate and jet of the flame ionisation detector, by three dry batteries wired in series. The ion current was amplified by a VIBRON ELECROMETER, model 33B-2 (E.I.L.), used in conjunction with an E.I.L. shunt unit, type A49A, which provided seven tenfold attenuations.

The circuit used in conjunction with the thermal conductivity detector is shown in Fig. 2. The values shown for the attenuator resistances are nominal values only: the attenuator was calibrated empirically. In Table 4 are listed the reciprocal sensitivities, used as multiplicative factors for conversion of peak area on a given range to the corresponding peak area on the most sensitive range (RANGE 1).

TABLE 1

CHROMATOGRAPHY CONDITIONS: SUMMARY

	Packing	Length (m)	Temp (°C)	Carrier	Flow (ml/min)
A	Silica Gel (40-60)	3	50	Hydrogen	25
B	Silica Gel (40-60)	$4\frac{1}{2}$	50	Hydrogen	75
C	Porapak-T	$1\frac{1}{2}$	40	Hydrogen	35
D	Porapak-T	$1\frac{1}{4}$	60	Helium	25
E	Alumina (100-120)	$4\frac{1}{2}$	60	Helium	25
F	Porapak-T + Porapak-Q	$1\frac{1}{4}$ + 3	50	Helium	25
G	Porapak-Q	$1\frac{1}{2}$	50	Hydrogen	25
H	Alumina (100-120)	$1\frac{1}{2}$	60	Hydrogen	50
I	Diethyl Adipate on Firebrick	10	0	Hydrogen	25
J	Porapak-T + Porapak-Q	3 + 3	50	Hydrogen	40

TABLE 2

SUBSTANCE	RETENTION TIMES (Mins) - Conditions (See Table 1) -										RELATIVE SENSITIVITIES	
	A	B	C	D	E	F	G	H	I	J	Th.C.D.	F.I.D.
Silane				2¾	3½	12						
Hexafluoroethane	6	3	4	4	9				2¾	10	1·29	0·62
Carbon Dioxide	9	4								11		
Ethylene										14	1·02	
Ethane			6			22	9			16½	1·14	8·79
Fluoroform	13	5	11	7½				2½	6	19	1·00	1·00
Perfluoropropane		8									1·57	
Pentafluoroethane		17									1·28	
Perfluoro-n-Butane		30									1·93	
Iso-Butane									15			
n-Butane								6	24		1·19	
1,1,1-Trifluoropropane								11			1·07	
But-1-ene									31			
trans But-2-ene									41			
cis But-2-ene									48			
1,1,1-Trifluoropentane									55			

FIG. 2. THERMISTOR DETECTOR CIRCUIT

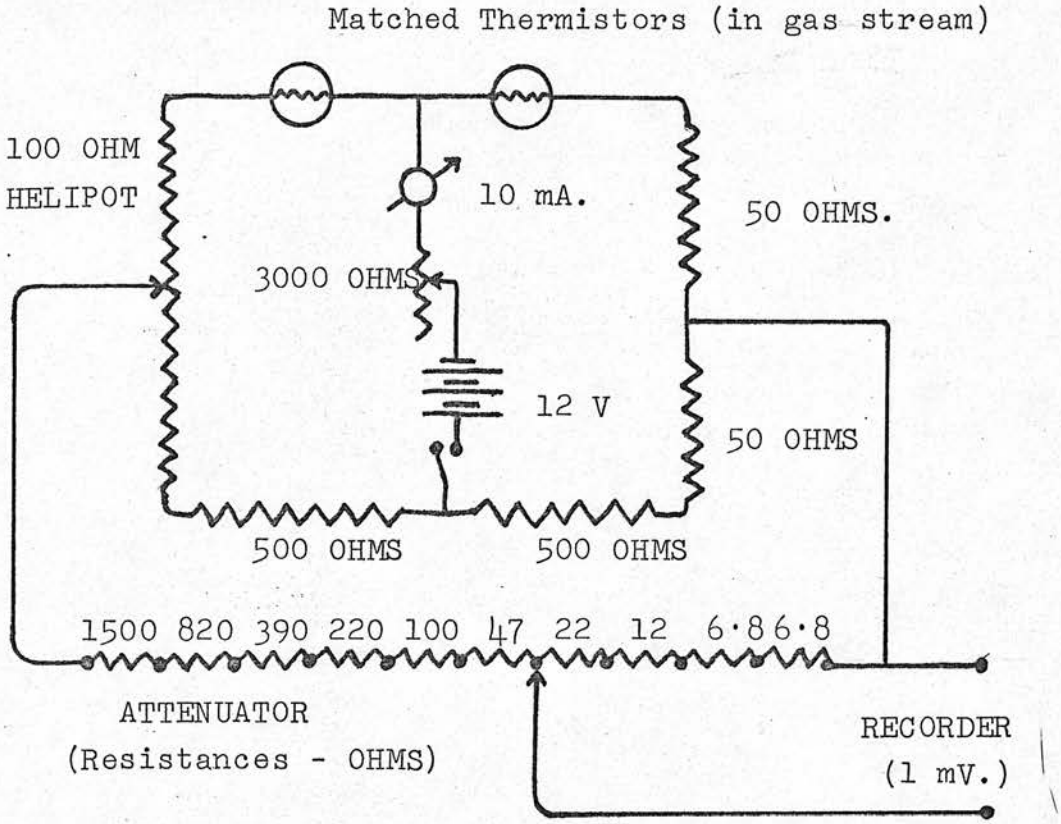


FIG. 3. FURNACE CIRCUIT

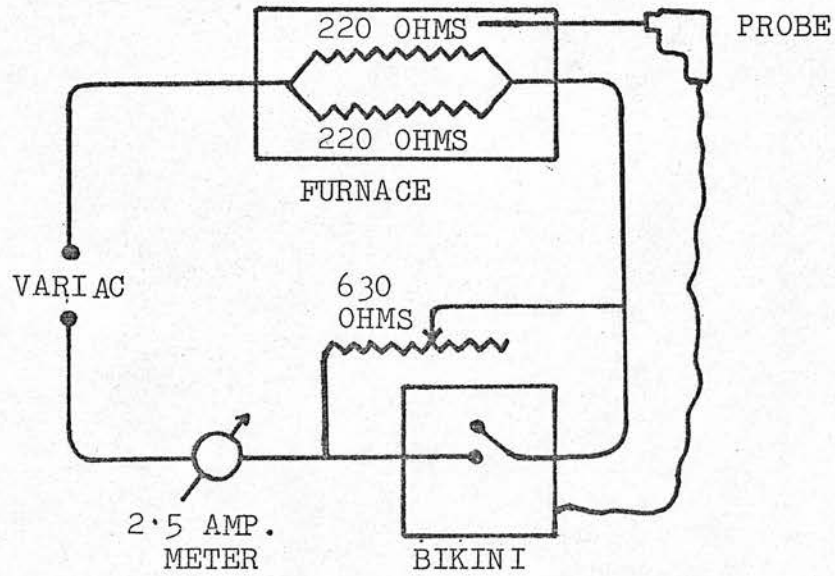


TABLE 3

TYPICAL CHROMATOGRAPHY CALIBRATION

Volume (cc)	Pressure (torr)	Temp. (°K)	Amount (micro moles)	Peak Area (sq.ins.)	Attenuator Range	Attenuator Factor	Area (sq.ins.) Range 1	Amount / Area
OA = ·0722	117	298	·455	8·03	1	1·000	8·03	·0566
OA = ·0722	182	299	·706	5·81	2	1·906	11·1	·0638
OB = ·624	68	297	2·29	8·52	3	3·764	32·1	·0713
OB = ·624	157	298	5·27	2·27	6	32·96	74·8	·0705
OB = ·624	233	298	7·82	7·03	5	16·14	114	·0688
OC = 2·16	165	299	19·1	4·55	7	64·28	293	·0566
OC = 2·16	253	298	29·4	7·08	7	64·28	455	·0646
							Mean =	·0658

The pressure of gas transferred to the u-tube is obtained directly from the difference in gas-burette readings before and after transfer.

(41)

CALIBRATION OF THERMISTOR DETECTOR

FIG. 4

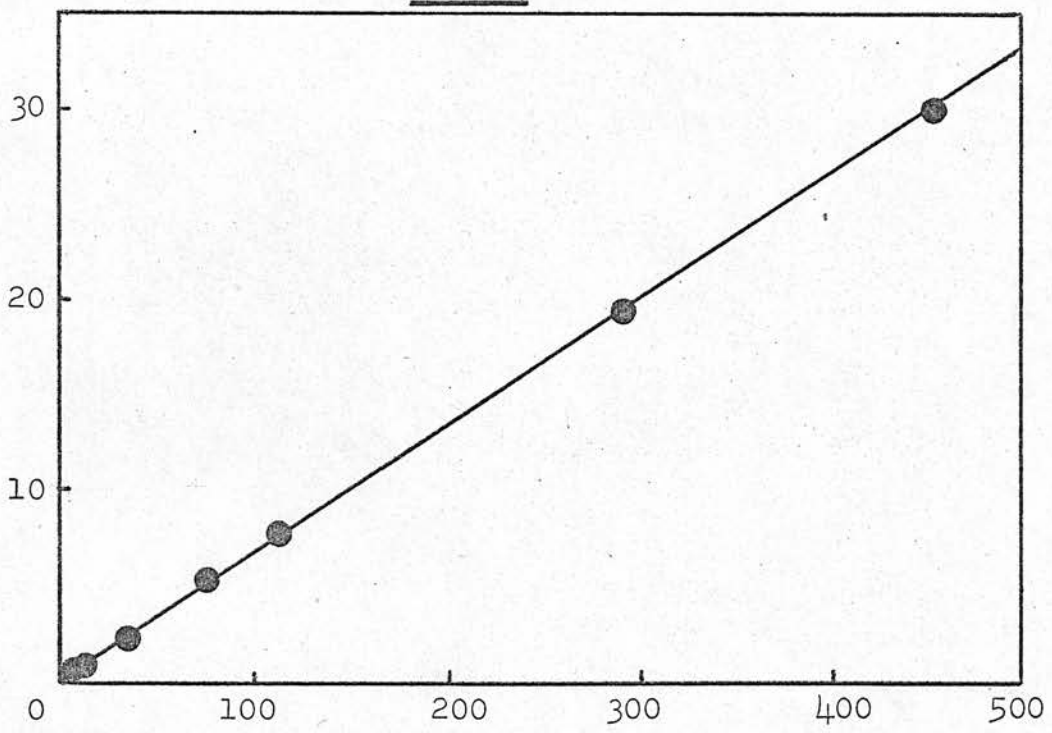


TABLE 4

THERMISTOR DETECTOR ATTENUATOR CALIBRATION

Range	Factor	Range	Factor
1	1·000	6	32·96
2	1·906	7	64·28
3	3·764	8	122·6
4	7·381	9	238·2
5	16·14	10	447·8

KENT 1 mv. recorders were used with both detectors. Peak areas were measured using an ALLBRIT fixed-arm planimeter.

Absolute calibration of either detector for a particular substance was achieved by measuring a sample in the gas-burette and transferring it quantitatively to the u-tube by Töpler pump.

TYPICAL CHROMATOGRAPHY CALIBRATION

The results of the calibration of the thermistor detector for fluoroform are detailed in Table 3 and presented graphically in Fig. 4. Since over this range there is obviously a linear relationship between peak area and amount of fluoroform, a mean value of AMOUNT/AREA is used as a conversion factor from peak area to yield.

Thus:

1 SQ. IN. (SCALE 1) = $(\cdot 066 \pm \cdot 002) \times 10^{-6}$ moles FLUOROFORM for a flow rate of 25 ml/min of HYDROGEN carrier and a thermistor detector current of 3 mA.

Although absolute calibrations were used in practice relative responses for a number of substances are listed in Table 2. The column headed Th.C.D. refers to the thermistor detector with HYDROGEN as carrier, while that headed F.I.D. refers to the flame-ionisation detector with air flowing at 750 ml/min (the standard flow-rate used throughout). Also shown in Table 2 are the absolute retention times of a number of substances under the various conditions listed in Table 1.

C. PHOTOLYSIS SYSTEM

(i) CELL

The reaction vessel was a quartz clyinder, (THERMAL SYNDICATE), of length 150 mm., and internal diameter 43 mm., with optically flat ends, and a side arm connected by graded seal to the pyrex vacuum system. The volume of the cylinder is 218 cc., while the side-arm and teflon stop-cock bring the total volume of the reaction vessel up to 222 cc.

(ii) FURNACE

The cell was housed in a heavy aluminium block furnace fitted with quartz end-plates. The temperature was controlled to within $\pm$ 0·2 C° using the circuit shown in Fig. 3. and measured using a mercury thermometer calibrated against the boiling points of a number of pure substances over the temperature range employed for runs.

(iii) OPTICS

The full arc from a 220W HANOVIA mercury lamp (housed in a metal box fitted with a shutter) was collimated by a quartz lens to produce a parallel beam of light which fully illuminated the cell.

2. PROCEDURE

Reaction mixtures were made up on a pressure basis, each reactant in turn being trapped into the mixing bulb at -196°C. Mixing was effected by immersing the bulb in hot water, a measured pressure of the reaction mixture was expanded into the cell, and the residue trapped back into the bulb. Photolysis times were controlled using the shutter on the lamp box, and measured by stop-watch. Where analysis for all products to be measured could be carried out on a single column, the contents of the cell after reaction were trapped directly into the u-tube of the chromatography injection system; otherwise they were transferred initially to trap (A). By partition between (A) and (B) product analysis could be performed on two different columns. Alternatively the contents of (A) could be separated by low-temperature distillation, fractions being transferred by Töpler pump to the u-tube for analysis by gas chromatography, to a sample tube for analysis by mass-spectrometer, or to the gas-burette for measurement prior to analysis by either method.

The low temperature sources used in this work are shown in Table 5.

TABLE 5

LOW TEMPERATURE SOURCES

Source	Temperature (°C)
ice/water	0
carbon tetrachloride slush	-23
chloroform slush	-63
acetone/cardice	-78
toluene slush	-95
n-propanol slush	-127*
iso-pentane slush	-160
liquid nitrogen	-196

* For most applications it was more satisfactory to use n-propanol slightly adulterated with iso-pentane, giving a temperature of about -130°C.

For thermal reactions runs were started by admitting the reactants to the cell, and stopped by trapping from the cell into (A) at -196°C. In systems involving deuterium labelling, the CF_3H and CF_3D formed were eluted together from the chromatography system, trapped out from the carrier gas by passage through a double loop of glass capillary at -196°C, and analysed by mass-spectrometer.

DARK REACTIONS

a) IN MIXING BULB

On mixing hexafluoroacetone with several of the hydrogen substrates studied, a marked reduction in total pressure was observed, and in some cases solid adducts were formed. For much of the work, therefore, trifluoromethyl iodide was used. This has the additional advantage of inhibiting secondary reactions. (See Chapter 3)

Before work was begun on a new substrate it was confirmed that no reduction in pressure occurred on mixing with the chosen radical source.

b) IN REACTION CELL

For each system involving a photolytic radical source at least one run was performed in which the normal run procedure was followed exactly, but the lamp was not unshuttered. In none of the systems studied was any dark reaction observed which led to the product measured.

3. CALCULATION OF RESULTS

A. INTERPRETATION OF MASS SPECTRA

Mass spectrometric analyses of gas mixtures were performed using an A.E.I. Ltd. MS-10 mass spectrometer. The data in Table 6 are taken from the manufacturers manual.

TABLE 6

CRACKING PATTERNS (Main peaks only)

Gas:	CH_4	CO	O_2	N_2
	13 : 7·69	12 : 4·49	16 : 11·4	14 : 7·18
	14 : 15·6	14 : 0·61	32 : 100	28 : 100
	15 : 85·8	16 : 0·95		
	16 : 100	28 : 100		
S:	3·9	3·8	2·6	3·6

(where S is the sensitivity w.r.t. principal peak)

Before analysis of any sample a background spectrum was run, each peak being subtracted from the corresponding peak in the sample spectrum.

1) ANALYSIS OF PERMANENT GASES

a) In runs where di-tertiary-butyl peroxide or acetone was used as methyl radical source, the fraction volatile at -196°C was analysed for methane, carbon monoxide and any traces of air. Assuming a nitrogen/oxygen ratio of 3·6 for air, it follows that the contribution to the 28 peak from carbon monoxide,

(CO^+) = 28 peak - 5·0 (32 peak) and

(CH_4^+) = 16 peak - 0·17 (32 peak) - 0·01 (CO^+)

$$\frac{(\text{METHANE})}{\text{CARBON MONOXIDE}} = \frac{(CH_4^+)}{(CO^+)} \times \frac{3\cdot8}{3\cdot9}$$

b) When azomethane was used as methyl radical source, analysis was made for methane, nitrogen and any traces of air.

In this case:

(N_2^+) from nitrogen = 28 peak - 5·0 (32 peak) and

(CH_4^+) = 16 peak - 0·17 (32 peak)

$$\frac{(\text{METHANE})}{(\text{NITROGEN})} = \frac{(CH_4^+)}{(N_2^+) \text{ from nitrogen}} \times \frac{3\cdot6}{3\cdot9}$$

2) ANALYSIS OF CF_3H/CF_3D MIXTURES

The 51 and 52 peaks may be accounted for as follows:

51 : CF_2H^+ 52 : $^{13}CF_2H^+$ and CF_2D^+

Since the normal ratio of isotopic abundances of ^{12}C and ^{13}C is 100 : 1·12, then assuming the same machine sensitivity for CF_3H and CF_3D,

$$\frac{(CF_3H)}{(CF_3D)} = \frac{(51)}{(52) - \cdot0112(51)}$$

B. TYPICAL RUNS

1. HYDROGEN ABSTRACTION BY TRIFLUOROMETHYL RADICALS

DATE: 30th April 1968

RUN NUMBER: 419

Pressure of H.F.A. in mixture = 112·6 torr (P_1)

Pressure of H.F.B.A. in mixture = 56·8 torr (P_2)

Total pressure = 169·4 torr

Pressure of mixture in cell = 68·0 torr (P_3)

(where H.F.A. is hexafluoroacetone and H.F.B.A. is heptafluorobutyraldehyde)

Furnace temperature, T = 126·8°C = 400·0°K

Photolysis time = 15 mins. = 900 secs.

CF_3H:

PEAK AREA = 3·19 sq. ins.

F = $2·268 \times 10^{-6}$ moles/sq.in.

C_2F_6:

PEAK AREA = 2·36 sq. ins.

F = $3·523 \times 10^{-6}$ moles/sq.in.

(where F = calibration factor)

Volume of cell = 222 cc.

Rate of formation of CF_3H = $\frac{3·19 \times 2·268 \times 10^{-6}}{222 \times 900}$

= $36·2 \times 10^{-12}$ moles $cm^{-3} sec^{-1}$

Rate of formation of C_2F_6 $= \frac{2\cdot36 \times 3\cdot523 \times 10^{-6}}{222 \times 900}$

$= 41\cdot61 \times 10^{-12}$ moles $cm^{-3} sec^{-1}$

$\sqrt{41\cdot61 \times 10^{-2}}$ $= \underline{6\cdot45 \times 10^{-6}}$

Pressure of H.F.B.A. in cell initially $= 68\cdot0 \times \frac{56\cdot8}{169\cdot4}$

Now, 760 torr, at $273\cdot2^{o}K$ = 1 mole per 22,400 cc.

$\therefore$ Initial conc^{n} of H.F.B.A. $= \frac{1}{22400} \times \frac{56\cdot8 \times 68\cdot0}{196\cdot4 \times 760} \times \frac{273\cdot2}{400\cdot0}$

$= \frac{56\cdot8 \times 68\cdot0}{169\cdot4} \times \frac{16\cdot05}{400\cdot0} \times 10^{-6}$

$= \cdot915 \times 10^{-6}$ moles cm^{-3}

ALDEHYDE USED = FLUOROFORM PRODUCED

$\therefore$ Change in H.F.B.A. conc^{n} during run

$= \frac{3\cdot19 \times 2\cdot268}{222} \times 10^{-6}$

$= \cdot032 \times 10^{-6}$ moles cm^{-3}

Mean concentration $= (\cdot915 - \cdot016) \times 10^{-6}$

$= \underline{\cdot899 \times 10^{-6}}$ moles cm^{-3}

Thus, using the relationship derived on page 26

$R = \frac{36\cdot2}{6\cdot45 \times \cdot899} = \underline{6\cdot25}$

$\frac{1000}{T} = \underline{2\cdot500}$ $\log_{10}R = 0\cdot796$

2. HYDROGEN ABSTRACTION BY METHYL RADICALS

DATE: 28th January 1969

RUN NUMBER: 568

Pressure of azomethane in mixture = 8·7 torr

Pressure of tetramethylsilane in mixture = 279·1 torr

Total pressure = 287·8 torr

Pressure of mixture in cell = 92·9 torr

Furnace temperature, T = 161·6°C = 434·8°K

Photolysis time = $2\frac{1}{4}$ mins = 135 secs.

$\underline{C_2H_6}$:

Peak Area = 3·26 sq. ins.

$F = 0{\cdot}0744 \times 10^{-6}$ moles/sq. in.

Amount of C_2H_6 formed = $3{\cdot}26 \times {\cdot}0744 \times 10^{-6}$

$= 0{\cdot}243 \times 10^{-6}$ moles

Initially:

(Azomethane) $= \frac{8{\cdot}7}{287{\cdot}8} \times \frac{92{\cdot}9}{1} \times \frac{16{\cdot}05}{434{\cdot}8}$ (as above)

$= 0{\cdot}104 \times 10^{-6}$ moles cm^{-3}

(Tetramethylsilane) $= \frac{279{\cdot}1}{287{\cdot}8} \times \frac{92{\cdot}9}{1} \times \frac{16{\cdot}05}{434{\cdot}8}$

$= 3{\cdot}325 \times 10^{-6}$ moles cm^{-3}

PRODUCTS VOLATILE AT -196°C

Volume : OA = ·0722 cm^3

Pressure = 161 torr

Temperature = 29°C = 302°K

Amount = $\frac{{\cdot}0722}{22400} \times \frac{273}{302} \times \frac{161}{760} = 0{\cdot}617 \times 10^{-6}$ moles

MASS SPECTRAL ANALYSIS

m/e	Background	Sample	Corrected Peak
16	1·4	563	562
28	21·7	1241	1219
32	0·0	3·2	3·2

It was shown on page 49 that (N_2^+) from nitrogen

= (corrected 28 peak) - 5 (corrected 32 peak)

= 1219 - 16 = 1203

(CH_3^+) = (corrected 16 peak) - 0·17 (corrected 32 peak)

= 562 - 0·6 = 561

$$\frac{(\text{Methane})}{(\text{Nitrogen})} = \frac{561}{1203} \times \frac{3·6}{3·9} = 0·430$$

$$\% \text{ Methane} = \frac{0·430}{1·430} = 30·1\%$$

Methane yield = ·617 x ·301 = $0·186 \times 10^{-6}$ moles

Nitrogen yield = ·617 x ·699 = $0·431 \times 10^{-6}$ moles

∴ Ethane formed in primary photolysis process

= ·431 x ·007 = $0·003 \times 10^{-6}$ moles

Ethane formed from combination of methyl radicals

= ·243 - ·003 = $\underline{0·240 \times 10^{-6}}$ moles

(Volume of cell = 222 cm^3)

Rate of formation of ethane by combination

$$= \frac{·240 \times 10^{-6}}{222 \times 135} = 8·01 \times 10^{-12} \text{ moles } cm^{-3} sec^{-1}$$

$$\sqrt{8·01 \times 10^{-12}} = 2·83 \times 10^{-6}$$

Total rate of formation of methane

$$= \frac{\cdot 186 \times 10^{-6}}{222 \times 135} = 6\cdot 21 \times 10^{-12} \text{moles cm}^{-3}\text{sec}^{-1}$$

R for abstraction of hydrogen from azomethane by methyl radicals = 4·0 at 161°C (See page 76)

Rate of formation of methane by abstraction from azomethane $= R \times (\text{azomethane}) \times \sqrt{\text{Rate of formation of ethane from radicals}}$

$$= 4\cdot 0 \times \cdot 104 \times 2\cdot 83$$

$$= 1\cdot 18 \times 10^{-12} \text{moles cm}^{-3}\text{sec}^{-1}$$

Rate of formation of methane by abstraction from tetramethylsilane $= 6\cdot 21 - 1\cdot 18$

$$= 5\cdot 03 \times 10^{-12} \text{ moles cm}^{-3}\text{sec}^{-1}$$

It is evident that the concentration of tetramethylsilane is effectively constant throughout the run, hence, using the relationship derived on page 26

$$R = \frac{5\cdot 03}{2\cdot 83 \times 3\cdot 325} = 0\cdot 535$$

$\frac{1{,}000}{T} = 2\cdot 300$ $\log_{10} R = \bar{1}\cdot 728$

4. MATERIALS

TRIFLUOROMETHYL IODIDE was obtained from two different sources.

a) Chromatographic analysis of the gas purchased from PIERCE CHEMICAL CO. revealed the presence of hexafluoroethane, fluoroform and carbon dioxide as impurities. These were removed by pumping at -130°C. The gas was then distilled at -63°C, and stored at -196°C in a blackened bulb on the vacuum line. It was further shown to be free from any hydrogen containing impurities by extensive photolysis of a sample of the iodide, when hexafluoroethane was formed in appreciable yield, but no measurable amount of fluoroform was produced.

b) Silver trifluoroacetate (KOCH-LIGHT) was intimately mixed with three times its own weight of iodine and heated, under slightly reduced pressure, with a free flame. The gases evolved were passed through a reflux condenser to remove most of the iodine vapour, and collected at -196°C. The fraction volatile between -63°C and -130°C was purified and stored as above.

$$CF_3COOAg + I_2 \longrightarrow CF_3I + AgI + CO_2$$

HEXAFLUOROACETONE was obtained from two different sources

a) Chromatographic analysis of the gas purchased from DU PONT CO. revealed the presence of hexafluoroethane, fluoroform, carbon dioxide, and a further impurity

tentatively identified as tetrafluoroethylene from its retention time. The gas was purified, stored, and the purity verified as in the case of the commercially obtained trifluoromethyl iodide.

b) Hexafluoroacetone sesquihydrate (KOCH-LIGHT) was dehydrated by dropping it onto a stirred mixture of phosphorus pentoxide and concentrated sulphuric acid at about 90°C. The gas evolved was trapped at -196°C, and the fraction volatile between -63°C and -130°C purified and stored as above.

TRIFLUOROACETALDEHYDE was prepared by dehydration of its hydrate (KOCH-LIGHT) using phosphorus pentoxide/ sulphuric acid mixture as above. The purity of the fraction volatile between -63°C and -130°C was established by comparison of its I.R. spectrum with that in the literature, (34) and by the absence of impurities (especially hexafluoroethane and fluoroform) as shown by chro matographic analysis.

PENTAFLUOROPROPIONALDEHYDE and HEPTAFLUOROBUTYRALDEHYDE were prepared from their hydrates. (EASTMAN-KODAK) and purified in the same way.

AMMONIA: Distilled anhydrous ammonia (99·98%, I.C.I. Agricultural Division) was distilled between -95°C and -130°C and used without further purification.

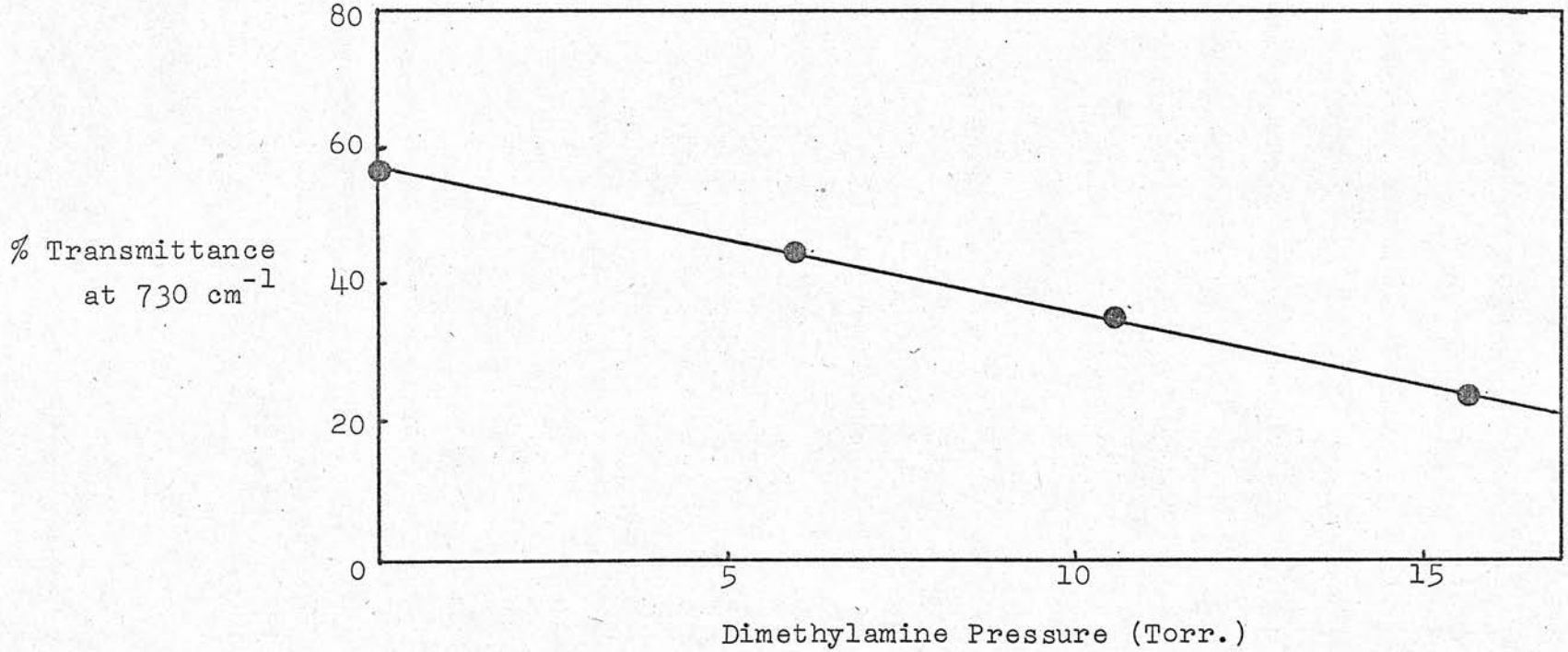
DIMETHYLAMINE-d was prepared by shaking 10 ml. of deuterium oxide, acidified with a few drops of hydrochloric acid, with 1 atmosphere of dimethylamine (B.D.H.) in a closed 1 litre bulb for 24 hours. The partially deuterated amine was distilled from the bulb, and the process repeated with a further 10 ml. of acidified heavy water. The amine was then distilled from the bulb (at room temperature) into a trap at -196°C, and the fraction volatile between -63°C and -95°C was trapped into a storage bulb on the vacuum line.

A gas-phase I.R. cell with sodium chloride end-plates was attached to the vacuum line by means of the B-14 cone, and pumped down. A measured pressure of undeuterated dimethylamine was admitted to the I.R. cell, and the transmittance at 730 cm^{-1} determined using an INFRACORD spectrometer. This procedure was repeated for a number of pressures, and a graph drawn of percent transmittance against pressure of dimethylamine in the cell. (Fig. 5) On deuteration the 730 cm^{-1} band shifts to 587 cm^{-1} (83), thus providing a means of determining the percentage exchange which has occurred.

The deuterated amine was then expanded into the storage, mixing and central manifolds, the I.R. cell, mixing bulb and reaction cell, and left to stand in the line for several days to allow exchange reactions between the amine and any hydrogen-containing substances adsorbed onto the walls of the vacuum system to reach equilibrium.

FIG. 5.

DEUTERATION OF DIMETHYLAMINE - CALIBRATION GRAPH
Variation of Transmittance at 730cm^{-1} with Pressure of Undeuterated Dimethylamine in I.R. Cell.



It was then trapped back into the storage bulb, thoroughly degassed, and a measured pressure expanded into the I.R. cell. The transmittance at 730 cm^{-1} was measured as before, and a second determination performed using a different pressure of amine in the cell. From the calibration graph the pressure of undeuterated amine in each sample could be determined, and hence the extent of deuteration was derived as shown below.

		PRESSURE (mm.) IN CELL	% TRANSMITTANCE AT 730 cm^{-1}
CALIBRATION WITH DIMETHYLAMINE		0·0	56
		6·0	45
		10·6	35
		15·7	24
DEUTERATED SAMPLE	a)	17·1	44
	b)	19·4	42

a) From calibration graph, pressure of dimethylamine (undeuterated) in cell = 6·35 mm.

therefore, % undeuterated = $\frac{6·35}{17·1}$ x 100 = 37·1%

b) From graph, pressure of dimethylamine in cell = 7·1 mm.

therefore, % undeuterated = $\frac{7·1}{19·4}$ x 100 = 36·6%

THUS:- DIMETHYLAMINE = 37% of sample, and

DIMETHYLAMINE-d = 63%

METHYLAMINE was prepared from the hydrochloride salt (B.D.H.) by dropping a saturated solution of caustic potash onto a saturated aqueous solution of the salt heated to about 80°C and stirred with a magnetic stirrer. The product was collected at -196°C, and the fraction volatile between -78°C and -130°C was again distilled between -95°C and -196°C to ensure that no traces of water remained.

TRIDEUTEROMETHYLAMINE was prepared from the hydrochloride (E. MERCK, A.G. DARMSTADT) in the same way. The isotopic purity of better than 99% was confirmed by mass-spectral analysis.

AZOMETHANE was prepared by the oxidation of sym-dimethyl-hydrazine with mercuric oxide. (5,6). Dimethylhydrazine hydrochloride (ALDRICH CHEMICAL Co.) was dissolved in the minimum amount of water, and neutralised to litmus by the addition of solid caustic potash. This solution was added dropwise to a magnetically stirred slurry of mercuric oxide in water, and the gas evolved was collected at -196°C. After the addition was completed, the temperature was raised to about 80°C to drive over dissolved azo-methane. The fraction volatile between -63°C and -130°C was stored at -196°C in a blackened bulb on the vacuum line. It was shown to be free from carbon dioxide and ethane by chromatographic analysis.

ETHANE purchased from B.O.C. was found to contain about 2% ethylene. This was removed by passing the gas through a column of bromine on charcoal. Traces of bromine were then removed by scrubbing with aqueous caustic soda, and the fraction volatile between -130°C and -196°C was collected. Chromatographic analysis revealed no impurities.

SILANE was prepared by dropping tetrachlorosilane (HOPKIN and WILLIAMS Ltd.) onto a stirred slurry of lithium aluminium hydride in diglyme at 0°C, under half an atmosphere of dry, oxygen-free nitrogen (B.O.C. 'spot' nitrogen passed through a column of molecular sieve). The product was passed through two traps at -78°C to remove solvent vapour, and collected at -196°C. The purity of the fraction volatile between -160°C and -196°C was verified by I.R., showing the absence of tetrachlorosilane, by mass spectroscopy, showing the absence of hydrogen chloride, carbon dioxide and nitrogen, and by gas chromatography which revealed no other impurities.

TRIMETHYLSILANE was similarly prepared by reduction of trimethylchlorosilane (HOPKIN and WILLIAMS Ltd.) at room temperature. The purity of the fraction volatile between -95°C and -130°C was verified by gas chromatography, I.R., and mass spectroscopy, as above.

The following commercial products were degassed and used without further purification.

n-BUTANE	MATHESON (C.P. GRADE)
ETHYLENE	" " "
BUT-1-ENE	" " "
cis-BUT-2-ENE	" " "
trans-BUT-2-ENE	" " "
FLUOROFORM	" " "
HEXAFLUOROETHANE	DU PONT
TRIDEUTEROMETHANOL	MERCK, SHARP and DOHME
METHANOL	B.D.H. (SPECTROSCOPIC GRADE)
CYCLOHEXANE	" " "
ACETONE	" " "
TETRAMETHYLSILANE	" (N.M.R. GRADE)
DIMETHYLAMINE	"
TRIMETHYLAMINE	"
ETHYLENEIMINE	KOCH-LIGHT
Di-tert-BUTYL PEROXIDE	" "

BENZIL (KOCH-LIGHT) and DIMETHYLFORMAMIDE (EASTMAN-KODAK) were used without purification.

In certain systems products occurred which were not readily available commercially, and for which there was no simple preparation. In order to obtain samples for calibration of the detector, such substances were trapped out from the chromatography carrier gas. This was done by passing the gas emerging from the thermal conductivity detector through a double loop of glass capillary, which was immersed in liquid nitrogen at the onset of the peak in question. After trapping, the samples were distilled between -63°C and -130°C in order to free them from water and carbon dioxide present in the carrier gas.

The following substances were prepared in this way:-

PENTAFLUOROETHANE

PERFLUORO-n-BUTANE

PERFLUOROPROPANE

1,1,1-TRIFLUOROPROPANE

CHAPTER 3

Hexafluoroacetone has been widely used as a photolytic source of $CF_3\cdot$ radicals. On mixing with methylamine, however, a white crystalline solid was immediately formed, while with trimethylamine a large drop in pressure occurred on mixing, an oily film being formed on the walls of the mixing vessel. Similar evidence of adduct formation was found when HFA was mixed with ammonia, dimethylamine, methanol and methyl mercaptan. Considerable reduction in pressure was also observed on mixing a small sample of hexafluoroazomethane with the above amines, and no further investigation of this radical source was undertaken.

CF_3I showed no sign of adduct formation with hydrocarbons, amines, alcohols, aldehydes, mercaptans, silanes, ethyleneimine or ammonia.

In order to assess its suitability as a radical source it was photolysed alone, and in the presence of cyclohexane. In the former case the only gaseous product detected was hexafluoroethane, which is consistent with the following simple reaction scheme.

$$CF_3I + h\nu \longrightarrow CF_3\cdot + I\cdot$$

$$CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6 \qquad (k_c)$$

$$I\cdot + I\cdot \rightleftharpoons I_2$$

$$CF_3\cdot + I_2 \longrightarrow CF_3I + I\cdot$$

$$CF_3\cdot + I\cdot \longrightarrow CF_3I$$

TABLE 7

Photolysis of TFMI in the Presence of CYCLOHEXANE

RUN	T(°K)	t (sec)	C_6H_{12}	TFMI	CF_3H	C_2F_6	R	1000/T	Log R
76	357·0	300	·272	1·75	14·4	1·88	38·5	2·80	1·586
55	357·1	300	·211	1·65	11·6	2·07	38·5	2·80	1·585
54	357·2	300	·250	1·92	14·7	2·30	38·9	2·80	1·589
53	370·3	600	·257	1·98	14·7	1·25	51·1	2·70	1·708
52	370·3	600	·265	1·96	15·1	1·20	52·0	2·70	1·716
47	370·3	1200	·235	1·41	11·0	·640	58·5	2·70	1·767
56	384·6	450	·193	1·51	17·2	1·23	80·6	2·60	1·906
57	385·1	300	·309	1·84	25·8	2·07	58·1	2·60	1·764
49	400·2	300	·331	1·69	37·1	1·44	93·5	2·50	1·970
48	400·0	1200	·214	1·29	16·7	·453	115	2·50	2·062
59	416·7	180	·158	1·80	33·7	2·33	139	2·40	2·144
58	416·7	300	·285	1·70	39·5	1·49	113	2·40	2·054
75	434·8	100	·238	1·53	75·3	2·51	200	2·30	2·300
60	434·8	100	·156	1·77	55·6	3·06	204	2·30	2·309
51	435·2	160	·240	1·77	63·6	1·67	205	2·30	2·312
50	434·7	300	·303	1·55	56·4	1·01	185	2·30	2·266

TABLE 8

Photolysis of HFA in the Presence of CYCLOHEXANE

Run	T(°K)	t (sec)	C_6H_{12}	HFA	CF_3H	C_2F_6	R	1000/T	Log R
77	357·0	60	·251	1·77	148	31·6	105	2·80	2·020
78	370·4	30	·238	1·68	263	50·1	156	2·70	2·193
73	400·3	60	·206	1·88	322	29·7	287	2·50	2·458
74	434·8	30	·184	1·68	664	48·8	525	2·30	2·712

C_6H_{12}, TFMI and HFA are in 10^{-6} mole cm^{-3}

CF_3H and C_2F_6 are in 10^{-12} mole $cm^{-3}sec^{-1}$

On addition of cyclohexane, fluoroform was also formed, and may be attributed to the reaction:

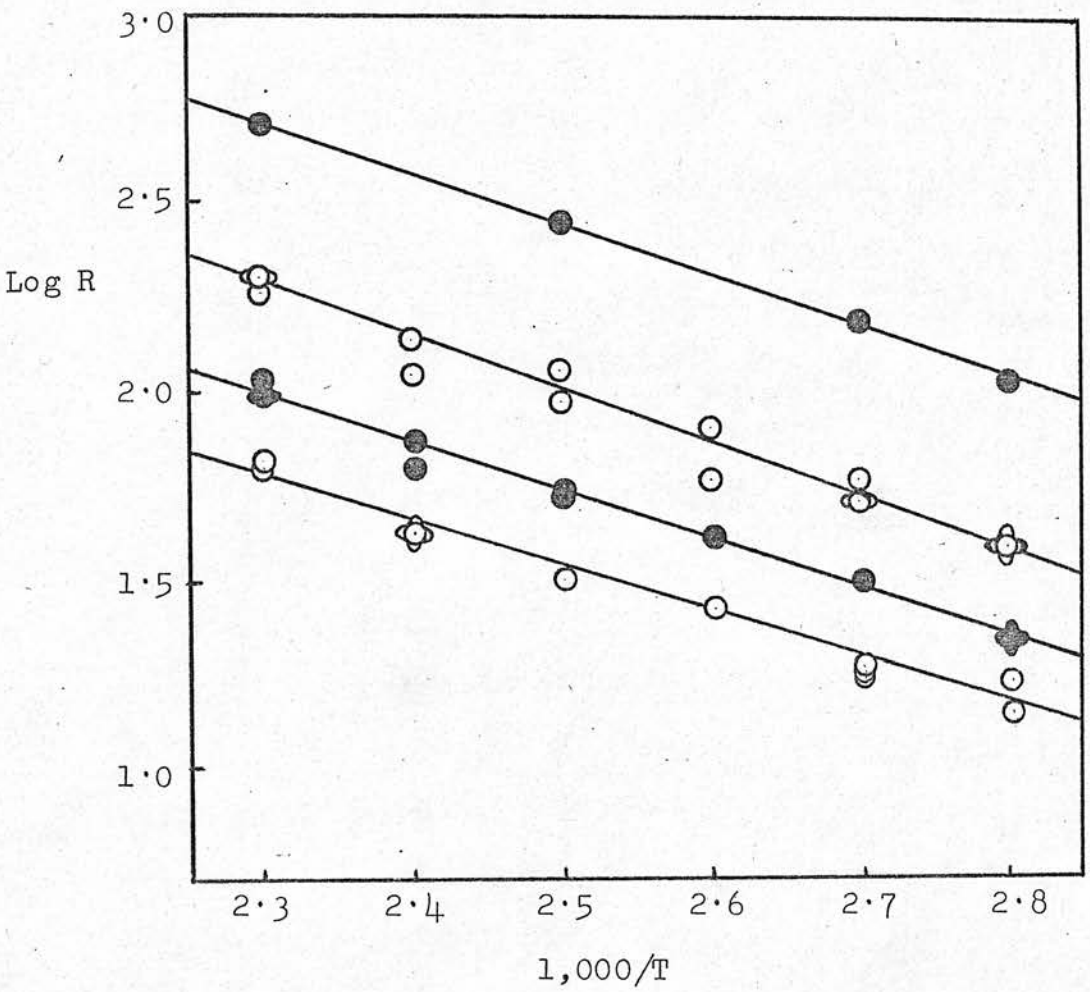
$$CF_3\cdot + C_6H_{12} \longrightarrow CF_3H + C_6H_{11}\cdot \quad (k_a)$$

The rate constants obtained for this reaction were in reasonable agreement with those previously reported by Charles and Whittle (62) using HFA as radical source. For internal consistency, however, a few runs were performed using the ketone and, as shown in Fig. 6 the rate constants obtained were higher than those from the iodide runs by an amount appreciably in excess of experimental error. In order to investigate this discrepancy further, it was decided to carry out a more extensive product analysis, to elucidate the mode of reaction of the alkyl radical formed by abstraction. Chromatographic analysis was complicated by the relatively high molecular weight of cyclohexane, and so n-butane was used. Again, as may be seen from Fig. 6, consistently higher rate constants were obtained when HFA was used as radical source.
The product distribution from a typical ketone run is shown below:-

HEXAFLUOROETHANE	8·9%
FLUOROFORM	68·8%
BUT-1-ENE	1·8%
trans-BUT-2-ENE	1·2%
cis-BUT-2-ENE	0·7%
$C_4H_9CF_3$ (total)	18·5%

FIG. 6.

CF_3 ATTACK ON HYDROCARBONS



● USING HFA AS RADICAL SOURCE
Upper Curve:- Cyclohexane
Lower Curve:- n-Butane.

○ USING TFMI AS RADICAL SOURCE
Upper Curve:- Cyclohexane
Lower Curve:- n-Butane.

TABLE 9

Photolysis of HFA in the Presence of n-BUTANE

Run	T(°K)	t(sec)	C_4H_{10}	HFA	CF_3H	C_2F_6	R	1000/T	Log R
159	357·1	45	·391	1·44	58·7	50·5	21·1	2·80	1·324
137	357·1	45	·586	1·66	65·9	29·1	20·9	2·80	1·320
160	357·1	180	·506	1·86	64·9	38·1	20·8	2·80	1·318
111	370·5	90	·724	·766	99·2	21·2	29·8	2·70	1·474
133	384·5	60	·415	1·89	117	50·1	39·9	2·60	1·601
136	400·0	45	·551	1·56	178	39·6	51·3	2·50	1·710
135	400·0	60·	·276	1·26	120	67·4	53·2	2·50	1·726
114	416·6	45	·980	·977	227	10·1	72·7	2·40	1·862
121	416·6	90	1·27	·570	176	5·10	61·4	2·40	1·788
134	434·6	45	·371	1·69	315	63·8	106	2·30	2·025
158	434·8	45	·318	1·17	262	71·0	98·0	2·30	1·991
138	434·9	60	·450	1·27	279	39·7	98·4	2·30	1·993

C_4H_{10} and HFA are in 10^{-6} mole cm^{-3}

CF_3H and C_2F_6 are in 10^{-12} mole $cm^{-3}sec^{-1}$

TABLE 10

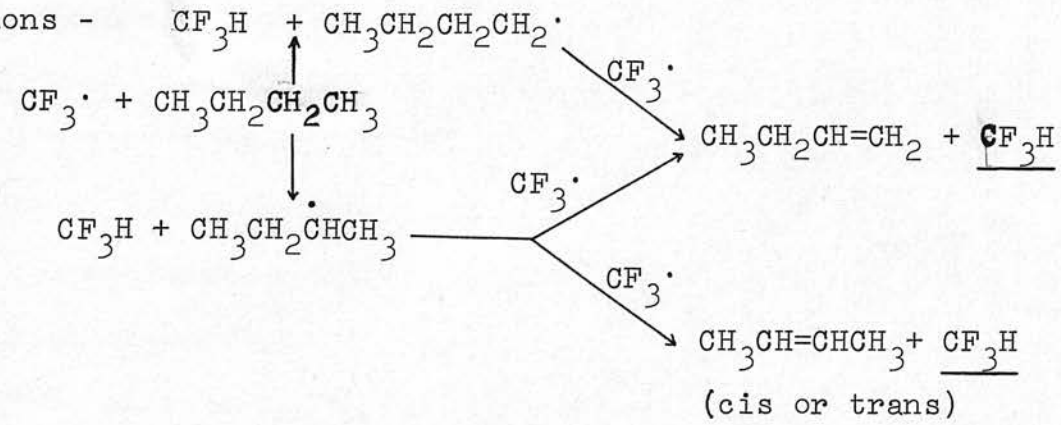
Photolysis of TFMI in the Presence of n-BUTANE

Run	T(°K)	t(sec)	C_4H_{10}	CF_3I	CF_3H	C_2F_6	R	1000/T	Log R
141	357·1	450	·419	1·58	7·78	1·27	16·5	2·80	1·218
142	357·2	900	·479	1·71	6·56	1·05	13·4	2·80	1·127
124	370·3	450	·162	1·99	5·80	4·31	17·3	2·70	1·238
115	370·3	450	·722	1·48	15·1	1·55	16·8	2·70	1·225
112	370·5	450	·841	·816	17·0	1·22	18·2	2·70	1·260
140	384·6	450	·439	1·65	12·5	1·22	25·7	2·60	1·410
143	400·2	450	·463	1·65	14·7	1·07	30·7	2·50	1·487
125	416·4	450	·145	1·79	11·2	3·56	41·4	2·40	1·617
113	416·6	180	·775	·752	41·9	1·75	40·9	2·40	1·612
116	416·7	200	·628	1·29	34·5	1·75	41·6	2·40	1·619
139	434·8	300	·410	1·54	30·3	1·41	62·3	2·30	1·795
144	434·9	450	·315	1·13	18·4	·804	65·1	2·30	1·814

C_4H_{10} and CF_3I are in 10^{-6} mole cm^{-3}

CF_3H and C_2F_6 are in 10^{-12} mole $cm^{-3}sec^{-1}$

This may be interpreted in terms of the following reactions -



$$C_4H_8 + CF_3\cdot \longrightarrow C_4H_8CF_3\cdot$$

$$C_4H_8CF_3\cdot \xrightarrow{C_4H_{10}} C_4H_9CF_3 + C_4H_9$$

$$C_4H_9\cdot + CF_3\cdot \longrightarrow C_4H_9CF_3$$

The reaction $C_4H_8 + CF_3\cdot \longrightarrow C_4H_7\cdot + CF_3H$ may also be of importance, particularly where an allylic hydrogen atom is involved. When TFMI is used as radical source, butene formation is inhibited, presumably by the reactions

$$C_4H_9\cdot + I\cdot \longrightarrow C_4H_9I$$

$$C_4H_9\cdot + I_2 \longrightarrow C_4H_9I + I\cdot$$

In consequence the additional sources of fluoroform indicated in the above reaction scheme are removed when CF_3I is used, leading to the observed difference in rate constants. It is evident that if every alkyl radical formed by abstraction lost a further hydrogen atom to form the corresponding olefin, rate constants calculated using

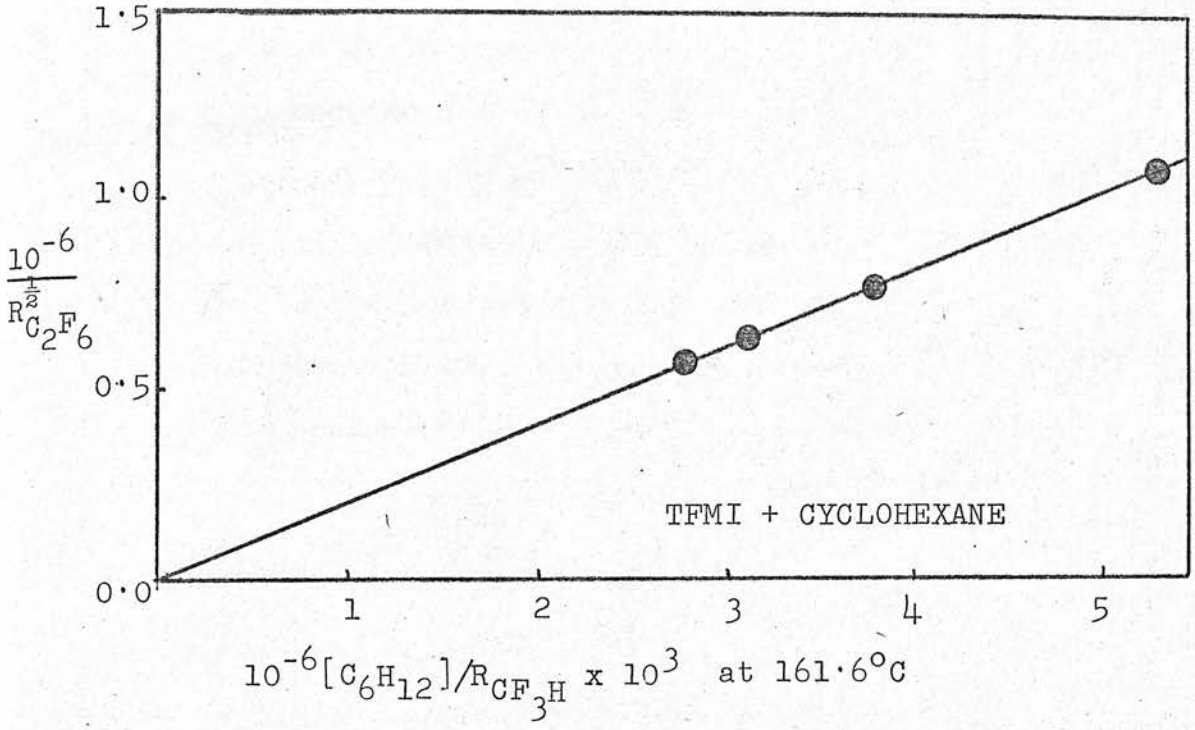
the total yield of fluoroform would be high by a factor of 2, but the activation energy would be unaffected. As will be seen from Tables 9 and 10, the observed factor for butane is around 1·4, indicating that the cross-disproportion/combination ratio for $C_4H_9\cdot$ and $CF_3\cdot$ is less than 1, while for cyclohexane (Tables 7 and 8) the ratio is around 2·7, which suggests further abstraction from cyclohexene. In neither case is the activation energy appreciably altered. It seems likely that most of the reported rate constants for hydrogen atom abstraction from alkanes using HFA (and presumably HFAM) will be high, but that the reported Arrhenius parameters are unlikely to be seriously affected. In systems where there is only one hydrogen atom in the substrate molecule, further reactions of the above type are not possible. Accordingly HFA was used as radical source only with the perfluoroaldehydes, TFMI being used in all other cases.

If direct abstraction from the hydrogen substrate RH is the only source of fluoroform, then,

$$R = \frac{k_a}{k_c^{\frac{1}{2}}} = \frac{R_{CF_3H}}{R_{C_2F_6}^{\frac{1}{2}}[RH]}$$

Thus a plot of $1/R_{C_2F_6}^{\frac{1}{2}}$ against $[RH] / R_{CF_3H}$ should be linear, passing through the origin. As will be seen from Figs. 7 and 8 this is in fact found to be the case for n-butane and cyclohexane using TFMI as radical source. The gradient of these plots corresponds to the mean value of R at the temperature chosen.

FIG. 7.



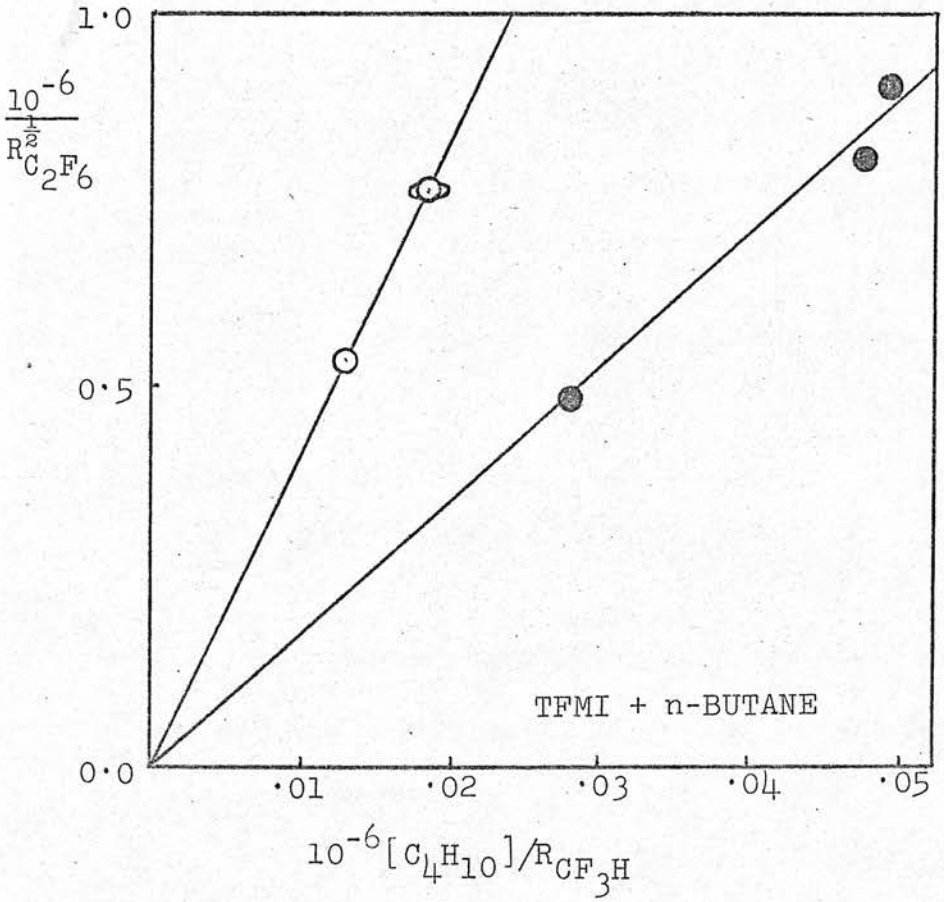


FIG. 8.

○ at 143·4°C

● at 97·2°C

As a further test of mechanism it may be verified that R is independent of run time (demonstrating that attack on products is unimportant), and of the relative concentrations of reactants. Whenever possible a ten-fold or greater variation in make-up and run time was used for each system studied. The available kinetic data for the reactions

$$n\text{-}C_4H_{10} + CF_3\cdot \longrightarrow C_4H_9\cdot + CF_3H \quad \text{and}$$
$$\text{cyclo-}C_6H_{12} + CF_3\cdot \longrightarrow C_6H_{11}\cdot + CF_3H$$

are summarised in Table 11 below.

It is convenient to compare rate constants at 164°C, since at this temperature 2·303RT = 2,000, and hence:

$$\log k_{164} = \log A - E/2 \quad (E \text{ is in kcal/mole})$$

TABLE 11

	E	log A	log k_{164}	Source	Ref.
n-Butane	5·74 ± ·28	11·31 ± ·16	8·4	TFMI	This work
	6·19 ± ·43	11·77 ± ·24	8·7	HFA	" "
	5·1	11·15	8·6	HFA	110
	5·3	11·46	8·8	HFAM*	60
Cyclohexane	6·39 ± ·28	12·16 ± ·16	9·0	TFMI	This work
	6·2	12·5	9·4	HFA	" "
	5·00	11·44	8·9	HFA	62

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^{-3}sec^{-1}$.

* Competitive study using $CF_3\cdot + D_2 \longrightarrow CF_3D + D\cdot$ as reference reaction.

Comparison with the corresponding parameters for methyl radicals (Table 12) shows the expected activation energy difference of around 3 kcal/mole, with little change in log A. In both cases log k_{164} is greater by 1·3 for trifluoromethyl radicals. At this temperature, therefore, abstraction of a secondary hydrogen atom from an alkane by $CF_3\cdot$ is about 20 times more rapid than the corresponding abstraction by $CH_3\cdot$.

TABLE 12

	TRIFLUOROMETHYL			METHYL RADICALS			
	E	log A	log k_{164}	E	log A	log k_{164}	Ref.
n-Butane	5·7	11·3	8·4	9·6	11·9	7·1	65 *
Cyclohexane	6·4	12·2	9·0	9·5	12·5	7·7	67

* CD_3 Radicals E is in kcal/mole, A and k_{164} in $mole^{-1}\ cm^3\ sec^{-1}$

It is possible that the presence of iodine in the system may affect the reaction scheme other than by removal of alkyl radicals. However, inhibition of butene formation when CF_3I is used indicates that the reactions

$$I\cdot + C_4H_9\cdot \longrightarrow HI + C_4H_8$$
$$\downarrow\ CF_3\cdot$$
$$CF_3H + I\cdot$$

do not occur to any appreciable extent. Reactions of the type: $RH + I\cdot \longrightarrow R\cdot + HI$ are also unlikely to be important, having far higher activation energies than the corresponding reactions of $CF_3\cdot$ e.g.

	E	log A	log k_{164}	Ref.
$CF_3\cdot + C_3H_8 \longrightarrow CF_3H + C_3H_7\cdot$	6·2	11·7	8·6	60
$I\cdot + C_3H_8 \longrightarrow HI + C_3H_7\cdot$	25·0	17·2	4·7	95

If hydrogen abstraction by iodine atoms did lead to the formation of appreciable amounts of fluoroform, then higher activation energy values would be expected, using TFMI. This is not the case, as will be seen from Figs. 5 and 6. The following simple reaction scheme is therefore proposed

$$CF_3I \underset{M}{\overset{h\nu}{\rightleftharpoons}} CF_3\cdot + I\cdot$$

$CF_3\cdot \xrightarrow{\frac{1}{2}C_2F_6}$ (removal)

$I\cdot \xrightarrow{\frac{1}{2}I_2}$ (removal)

$$CF_3\cdot + RH \longrightarrow CF_3H + R\cdot$$

$$R\cdot + I\cdot \longrightarrow RI$$

$$R\cdot + I_2 \longrightarrow RI + I\cdot$$

This mechanism cannot, of course, be applied uncritically to systems where RH is not a hydrocarbon. In each case therefore, the mechanism was tested by studying the effect on R of variations in run time, make-up, and $CF_3\cdot$ concentration.

In the course of this work, hydrogen abstraction by methyl radicals from a number of substrates has also been studied. Azomethane is a convenient and widely used photolytic source of methyl radicals. Its decomposition takes place by the following mechanism:-

$$CH_3N_2CH_3 + h\nu \longrightarrow 2CH_3\cdot + N_2$$

$$CH_3N_2CH_3 + h\nu \longrightarrow C_2H_6 + N_2$$

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6 \qquad (k_c)$$

$$CH_3\cdot + CH_3N_2CH_3 \longrightarrow CH_4 + CH_3N_2CH_2\cdot \qquad (k_a)$$

$$CH_3\cdot + CH_3N_2CH_3 \longrightarrow (CH_3)_2\dot{N}_2CH_3 \xrightarrow{CH_3\cdot} (CH_3)_2N_2(CH_3)_2$$

TABLE 13.

AZOMETHANE PHOTOLYSIS

Run	T(°K)	t(sec)	AZO	N_2	C_2H_6	CH_4	R	1,000/T	log R
493	526·3	135	1·84	395	48·4	223	17·4	1·90	1·241
503	526·3	135	0·741	186	41·7	95·1	19·9	1·90	1·298
498	344·8	135	7·62	579	412	63·1	·408	2·90	$\bar{1}$·611
500	344·8	450	2·74	275	237	19·2	·455	2·90	$\bar{1}$·658
501	344·8	45	1·37	165	163	6·44	·367	2·90	$\bar{1}$·565

The azomethane concentration, AZO, is in 10^{-6} mole cm^{-3}

N_2, C_2H_6 and CH_4 are in 10^{-12} mole $cm^{-3} sec^{-1}$

Mean R at 526·3°K = 18·7 $\therefore$ Log $R_{526·3}$ = 1·272

Mean R at 344·8°K = ·410 $\therefore$ Log $R_{344·8}$ = $\bar{1}$·613

$\therefore$ Gradient of Arrhenius Plot = (1·272 - $\bar{1}$·613)/(1·9 - 2·9) = -1·659

$\therefore$ Intercept on Log R axis = 1·272 + 1·9 (1·659) = 4·424

$\therefore$ Log A = 4·42 + 6·68 = <u>11·10</u>

E = 2·303R x 1·659 = <u>7·59</u> kcal/mole.

Taking the quantum yield of nitrogen as unity, that for ethane formed by intramolecular elimination is about 0·007 (6) and the total yield of ethane must be corrected for this before calculating the $CH_3\cdot$ concentration.

In the above scheme k_a is high, and abstraction from the radical source makes a large contribution to the total yield of methane for most hydrogen substrates. Accordingly the photolysis was studied briefly to provide internally consistent correction factors (Table 13), the Arrhenius parameters obtained being in agreement with those of previous workers (Table 14).

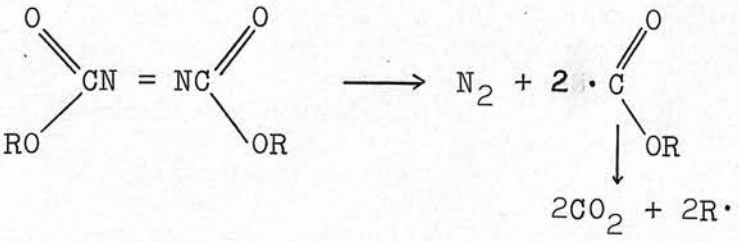
TABLE 14

	E	Log A	Log k_{164}	Ref.
$CH_3\cdot + CH_3N_2CH_3 \longrightarrow CH_4 + CH_3N_2CH_2\cdot$	7·6	11·1	7·3	This work
	7·9	11·0	7·0	96
	8·7	11·5	7·1	97
(E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$)	7·8	10·9	7·0	98
	7·8	11·0	7·1	100

In investigating hydrogen atom abstraction from perfluoroaldehydes by methyl radicals, di-tertiary-butyl peroxide (DTBP) was used. Being a thermal source, photolysis of the aldehydes was eliminated. k_a for DTBP is considerably lower than for R_fCHO, and abstraction from the radical source made little contribution to the methane formed. Accordingly the photolysis of DTBP was not studied, established parameters for the following reaction being used. $(CH_3)_3O_2(CH_3)_3 + CH_3\cdot \longrightarrow CH_4 + (CH_3)_3O_2(CH_3)_2CH_2\cdot$

E = 11·9 kcal/mole, Log A = 12·7 (A is in $mole^{-1}cm^3sec^{-1}$)(109)

Photolysis or thermal decomposition of the esters of azodiformic acid would at first sight appear to offer a useful source of alkyl and alkoxycarbonyl radicals.



If the above reaction scheme is obeyed then:-

$$CO_2/N_2 = 2 \quad \text{and} \quad \sum R\cdot/CO_2 = 1$$

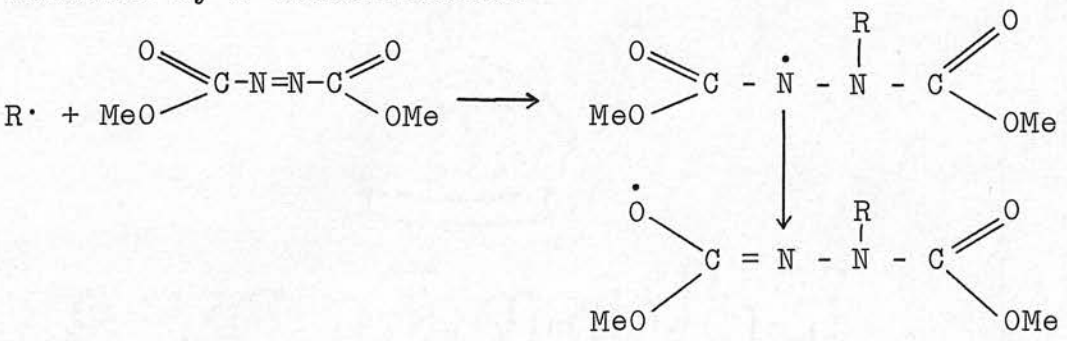
Jones and Thynne studied the gas-phase thermal decomposition of Dimethyl Azodiformate at 162°C and found ratios of about 0·94 and 0·06 respectively. Thus less than half the methoxycarbonyl radicals formed decomposed, while auto-combination accounts for as little as 6% of the methyl radicals formed (no methane being detected). In the present work this discrepancy between observed and predicted ratios was investigated by analysis of the products formed on photolysing M/100 solutions of dimethylazodiformate in dodecane. Under these conditions the characteristic red colour of the ester disappeared rapidly, although the yield of nitrogen indicated less than 10% decomposition, the solution becoming a viscous gel. On pumping off the solvent, and extracting with dimethylformamide (DMF), a semi-solid polymer-like substance remained, which contained:-

44·1% CARBON, 12·6% NITROGEN, 6·4% HYDROGEN.
and 36·8% OXYGEN (by difference).

The mean molecular weight was determined using a MECHROLAB Vapour Pressure Osmometer. Solutions ranging from

50 to 4 g/l were made up with DMF as solvent and Benzil solutions of comparable strength were used to calibrate the instrument. The molecular weight was found to be 520 ± 50, the error limit representing the spread of results from several determinations on different polymer samples.

These results may be interpreted in terms of addition of methyl and methoxycarbonyl radicals to the azo linkage, followed by a isomerisation:-



The radical thus formed may then react by further addition to the azodiformate. The observed molecular weight suggests an average of about three azodiformate units per polymer molecules. The low nitrogen yield and rapid bleaching are both explained by this mechanism, while it is evident that most of the methyl, and about half the methoxycarbonyl, radicals formed react by addition. The decomposition of azodiformate esters is not, therefore, likely to prove useful as a radical source.

CHAPTER 4.

When this work was started, virtually no quantitative kinetic data had been reported for free-radical reactions involving silicon compounds (101). The reactions of silanes, which in many respects are analogous to those of hydrocarbons, often occur with greater violence or under milder conditions. For example the oxidation of silane

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

occurs spontaneously at room temperature. Although the mechanism of combustion reactions has yet to be established unequivocally, it is generally agreed that the initial attack takes the form of a hydrogen abstraction, probably by $HO_2\cdot$.

$$\text{e.g. } CH_4 + HO_2\cdot \longrightarrow CH_3\cdot + H_2O_2$$

This suggests that the activation energy for hydrogen abstraction from silanes is lower than that for hydrocarbons, indicating the Si-H bond strength to be less than that of a C-H bond in a similar molecule environment. The first systematic study of hydrogen abstraction from molecules containing silicon was made by Kerr and his co-workers (98, 99) who reacted methyl radicals with a number of substituted silanes. Their results are summarised in Table 15. These results suggest that the observed high rates of reaction are due, not to low activation energies, but to high A-factors, which the authors attributed to ionic complex formation during the transition state.

TABLE 15.

	E	Log A	Log k_{164}
$CH_3\cdot + F_3SiH \longrightarrow CH_4 + F_3Si\cdot$	8·7	12·4	8·0
$CH_3\cdot + Cl_3SiH \longrightarrow CH_4 + Cl_3Si\cdot$	8·5	13·4	9·1
$CH_3\cdot + MeCl_2SiH \longrightarrow CH_4 + MeCl_2Si\cdot$	7·2	12·9	9·3
$CH_3\cdot + Me_3SiH \longrightarrow CH_4 + Me_3Si\cdot$	7·0	11·1	7·6
$CH_3\cdot + ClSiMe_3 \longrightarrow CH_4 + ClSiMe_2CH_2\cdot$	11·5	13·4	7·6
$CH_3\cdot + Cl_2SiMe_2 \longrightarrow CH_4 + Cl_2SiMeCH_2\cdot$	11·6	13·2	7·4
$CH_3 + Cl_3SiMe \longrightarrow CH_4 + Cl_3SiCH_2$	11·5	12·9	7·1

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$.

In a recent re-investigation of hydrogen abstraction from trichlorosilane, however, Kerr (103) obtained the following Arrhenius parameters:-

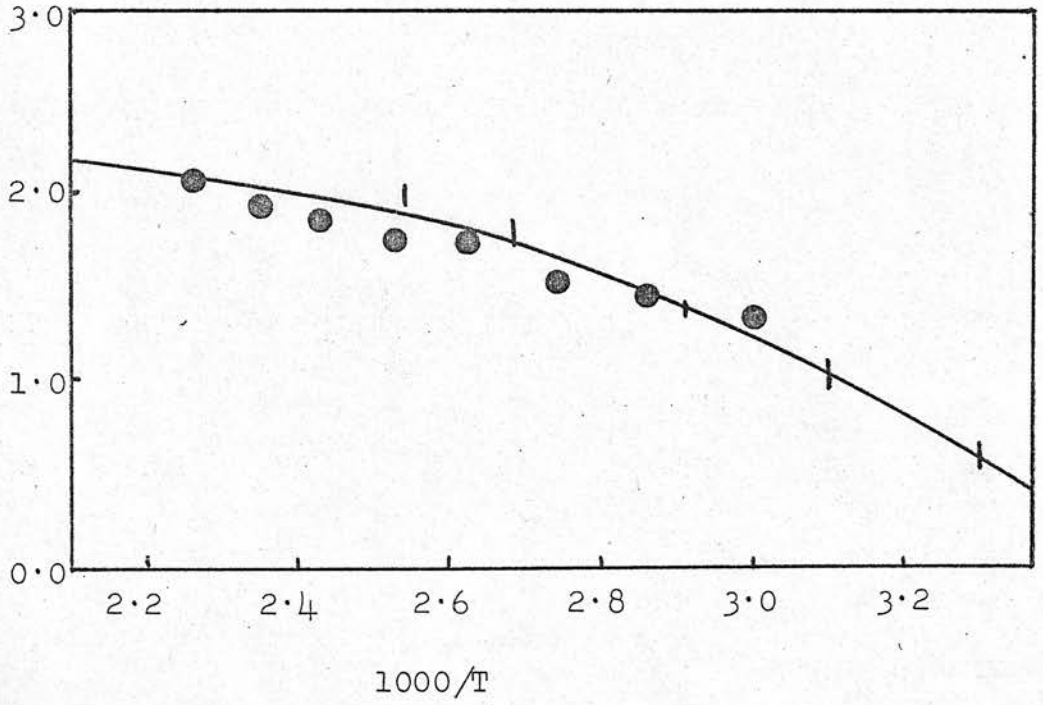
E = 4·3 kcal/mole, Log A = 10·8,

the activation energy being almost half that previously reported. In Fig. 9 the results of these two studies are shown as a single Arrhenius plot, which appears to exhibit distinct curvature. It seems, therefore, that in the case of the halosilanes, the reaction mechanism may be more complex than suspected, and that little confidence should be placed in the high A-factors reported.

In the present work the reactions of methyl and trifluoromethyl radicals with silane, trimethylsilane and tetramethylsilane have been studied: the results are recorded in tables 16 to 21 and presented graphically in Figs. 10 to 14. Since the beginning of this year (1969) a considerable quantity of kinetic data has become available for the abstraction of hydrogen from group IV tetramethyls. This is summarised in Table 22.

REPORTED ARRHENIUS PARAMETERS FOR THE REACTION:-

$$CF_3\cdot + Cl_3SiH \longrightarrow CF_3H + Cl_3Si\cdot$$



BLACK CIRCLES indicate the results of KERR, STEPHENS and YOUNG (103)

VERTICAL BARS show the range of values obtained at each of five temperatures by KERR, SLATER and YOUNG (98).

FIG. 9.

RUN	T(°K)	t(sec)	AZO	SILANE	N_2	C_2H_6	CH_4 (AZO)	CH_4 (SILANE)	R	$\frac{1000}{T}$	Log R
565	370·4	135	·108	3·46	15·1	13·3	·342	·682	·0542	2·70	$\bar{2}$·734
570	400·0	450	·118	3·80	14·5	9·91	·69	1·75	·147	2·50	$\bar{1}$·167
568	434·8	135	·104	3·33	14·0	8·11	1·18	5·03	·535	2·30	$\bar{1}$·728
560	476·2	45	·324	3·31	63·8	18·5	12·0	33·8	1·55	2·10	0·191
569	526·3	450	·145	4·65	30·6	2·03	3·7	21·5	3·42	1·90	0·535
567	526·3	135	·087	2·79	23·7	2·27	2·4	13·0	3·23	1·90	0·509
580	322·6	450	1·99	2·02	181	117	4·1	65·1	2·99	3·10	0·477
571	344·8	135	3·40	1·13	334	261	22	104	5·73	2·90	0·758
572	344·8	45	4·62	1·54	479	466	41	172	5·19	2·90	0·715
577	344·8	450	2·04	·679	243	190	11·5	56·1	6·01	2·90	0·779
573	370·4	90	3·49	1·16	360	186	41	175	11·1	2·70	1·045
587	400·0	225	2·66	·224	291	114	52	62	24·6	2·50	1·392
584	434·8	450	1·64	1·66	193	11·2	21	214	41·2	2·30	1·614
585	476·2	480	1·29	1·31	222	5·12	21	224	90·6	2·10	1·962
586	476·2	225	2·86	·255	346	27·0	129	133	100	2·10	2·017

TABLE 16

$Me_4Si + CH_3\cdot$

TABLE 17

$SiH_4 + CH_3\cdot$

(Units under)
(Table 18)

TABLE 18

Photolysis of Azomethane in the Presence of Trimethylsilane

RUN	T(°K)	t(sec)	AZO	SILANE	N_2	C_2H_6	CH_4 (AZO)	CH_4 (SILANE)	R	$\frac{1000}{T}$	Log R
504	344·8	135	·115	1·24	22·7	25·6	0·23	3·44	·551	2·90	$\bar{1}$·741
505	370·4	135	·236	2·54	43·0	31·8	1·2	14·8	1·02	2·70	0·008
511	370·4	135	·497	1·73	70·7	56·1	3·3	15·2	1·17	2·70	0·070
512	370·4	135	1·01	1·02	127	102	9·1	11·2	1·09	2·70	0·036
508	400·0	135	0·589	2·05	89·3	48·7	7·8	38·6	2·70	2·50	0·431
509	434·8	45	0·380	1·32	59·0	29·0	8·1	36·7	5·17	2·30	0·714
506	476·2	90	0·151	1·62	32·6	3·72	1·8	39·2	13·0	2·10	1·114
482	500·0	50	0·724	1·66	153	20·1	39	117	16·1	2·00	1·207
483	500·0	500	0·500	1·15	99·2	8·38	17·4	69·8	21·9	2·00	1·340
507	526·3	135	0·110	1·18	34·0	2·24	3·0	46·5	28·0	1·90	1·447

The concentrations, AZO and SILANE, are in 10^{-6} mole cm^{-3}, the rates of formation of nitrogen, ethane and methane (formed by abstraction from azomethane or from the silane) are given in 10^{-12} mole $cm^{-3} sec^{-1}$.

TABLE 19

Photolysis of TFMI in the Presence of Silane

RUN	T(°K)	t(sec)	S	TFMI	CF_3H	C_2F_6	R	$\frac{1000}{T}$	Log R
592	312·5	450	1·00	1·01	37·0	0·851	40·5	3·20	1·607
604	327·9	3600	0·674	0·687	12·9	0·065	77·7	3·05	1·890
601	344·8	4500	0·159	2·03	5·97	0·198	92·2	2·90	1·965
594	344·8	900	0·557	0·565	16·9	0·110	92·8	2·90	1·967
595	344·8	900	0·372	1·40	38·9	0·981	111	2·90	2·044
603	370·4	3600	0·521	0·532	23·6	0·084	171	2·70	2·232
596	400·0	900	0·311	1·17	82·6	1·33	262	2·50	2·418

TABLE 20

Photolysis of TFMI in the Presence of Trimethylsilane

RUN	T(°K)	t(sec)	TMSH	TFMI	CF_3H	C_2F_6	R	$\frac{1000}{T}$	Log R
530	322·6	150	0·650	2·06	57·9	1·80	66·9	3·10	1·825
517	344·8	150	0·991	0·936	108	0·98	110	2·90	2·043
520	344·8	150	0·247	2·21	43·2	2·14	121	2·90	2·083
532	370·4	650	0·564	1·79	136	1·44	218	2·70	2·338
525	370·4	45	0·284	2·54	183	8·20	228	2·70	2·358
522	400·0	150	0·209	1·87	114	2·68	346	2·50	2·539
526	434·8	250	0·664	2·19	515	2·04	601	2·30	2·778
523	476·2	150	0·242	2·17	479	3·69	1210	2·10	3·082

Concentration of silane, S, trimethylsilane, TMSH, and TFMI are in 10^{-6}mole cm^{-3}, CF_3H and C_2F_6 are in 10^{-12}mole $cm^{-3}sec^{-1}$.

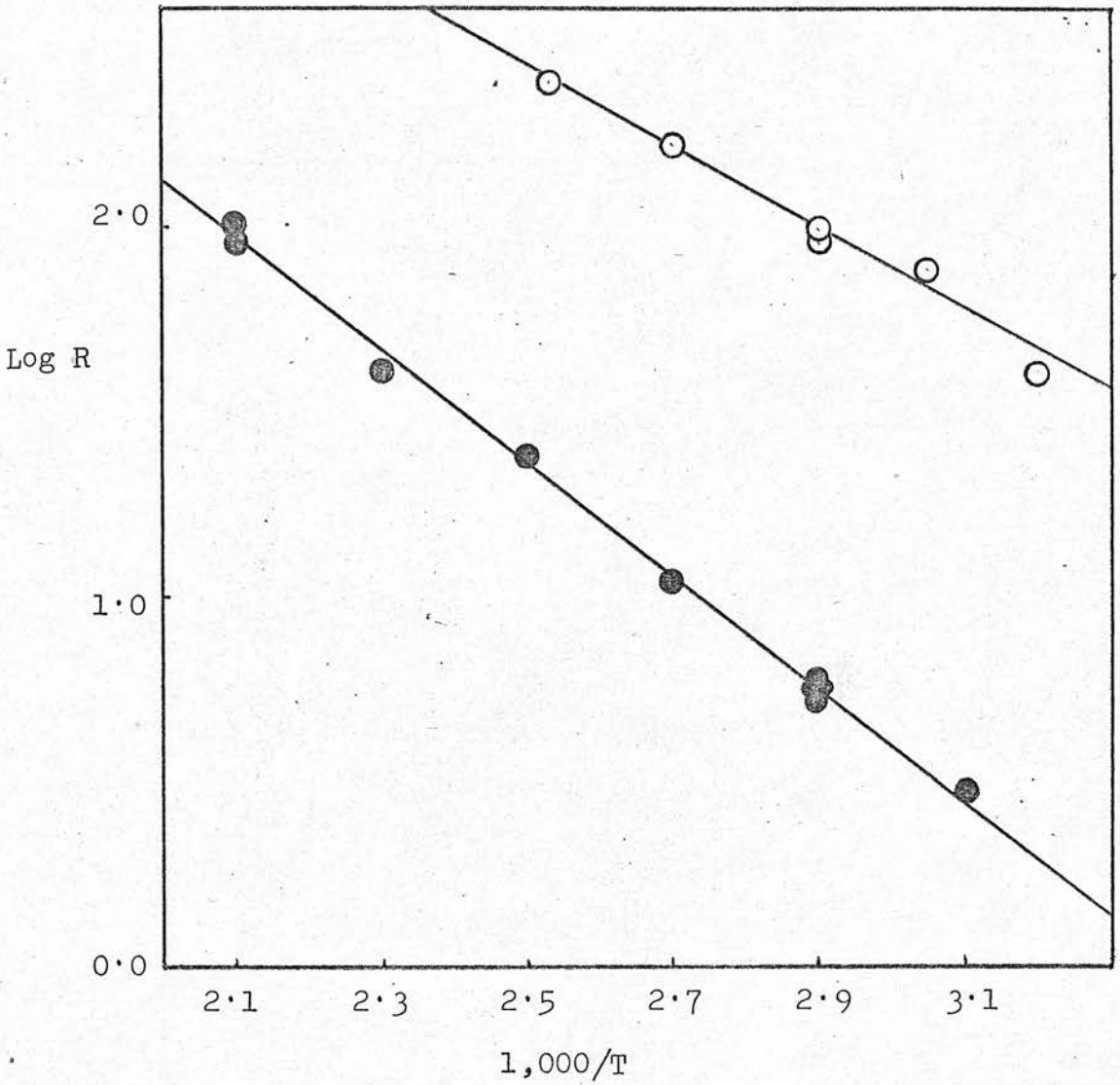
TABLE 21

Photolysis of TFMI in the Presence of Tetramethylsilane

RUN	T(°K)	t(sec)	TMS	TFMI	CF_3H	C_2F_6	R	1000/T	Log R
547	344·8	1500	0·141	1·43	0·426	0·706	3·61	2·90	0·558
545	344·8	1800	0·250	2·55	0·663	0·762	3·04	2·90	0·483
536	370·4	900	0·600	2·05	3·57	0·841	6·51	2·70	0·813
538	370·4	3600	0·623	2·13	2·44	0·328	6·88	2·70	0·837
539	370·4	360	0·644	2·20	5·84	1·59	7·21	2·70	0·858
548	400·0	1800	1·29	1·29	9·56	0·365	12·4	2·50	1·092
551	434·8	3600	1·22	1·22	16·7	0·160	35·1	2·30	1·545
542	476·2	2400	0·251	2·56	11·4	0·686	58·0	2·10	1·763
541	476·2	2400	0·460	1·57	12·9	0·166	71·3	2·10	1·853
550	476·2	1200	1·33	1·33	42·8	0·209	72·0	2·10	1·857
544	526·3	450	0·242	2·47	46·9	1·68	156	1·90	2·193

Concentration of tetramethylsilane, TMS, and TFMI in 10^{-6} mole cm^{-3}, CF_3H and C_2F_6 in 10^{-12} mole $cm^{-3}sec^{-1}$.

FIG. 10. HYDROGEN ABSTRACTION FROM SILANE



$$SiH_4 + CF_3\cdot \longrightarrow SiH_3\cdot + CF_3H$$

$$SiH_4 + CH_3 \longrightarrow SiH_3\cdot + CH_4$$

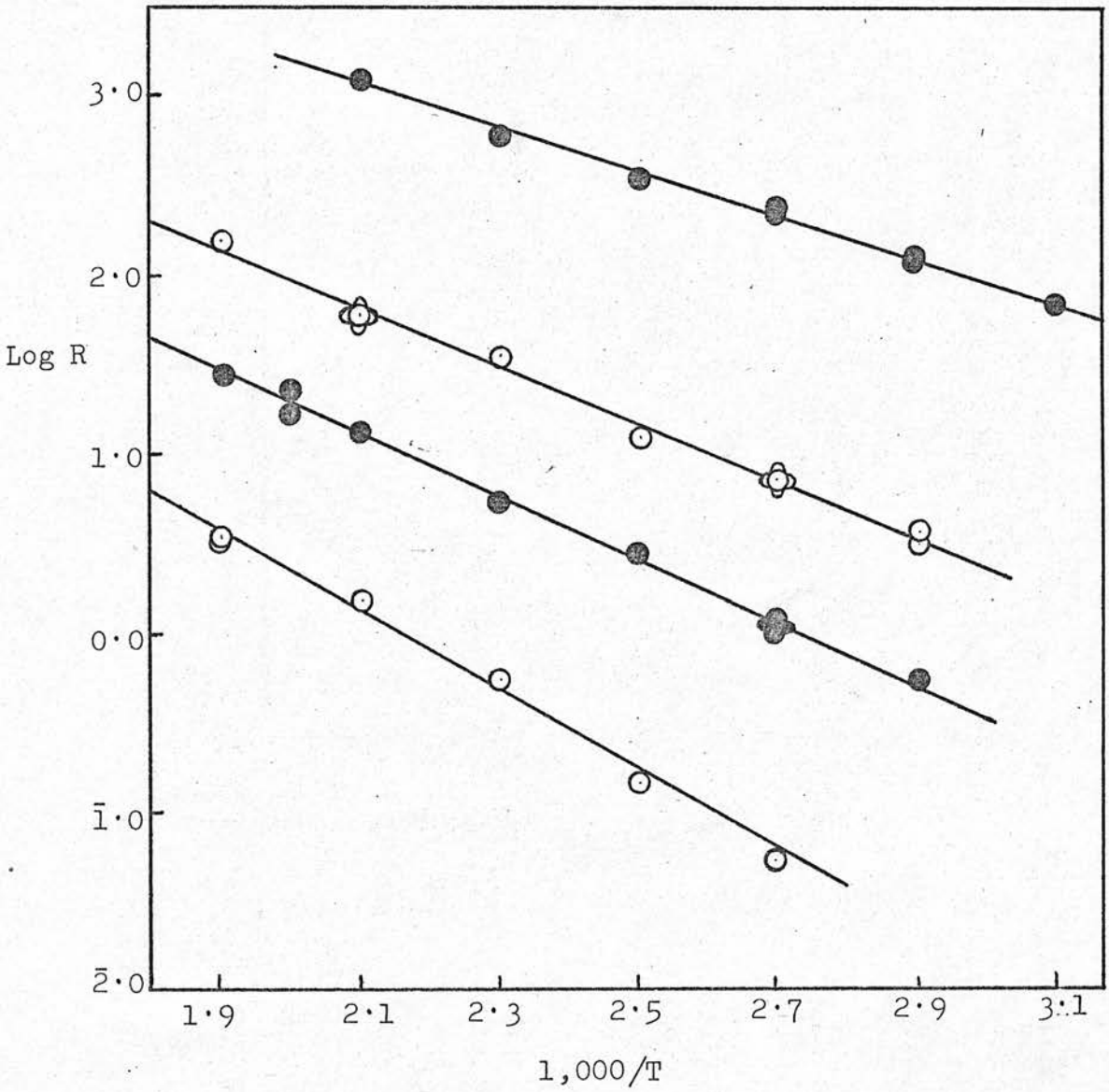
NOTE: Since the completion of the text of this Thesis, Arrhenius Parameters have been reported for the methyl radical reaction, which are in excellent agreement with those obtained in the present work.

Ref 155: $E = 7{\cdot}0 \pm {\cdot}6$ $\quad \text{Log } A = 11{\cdot}8 \pm {\cdot}3$

This work: $E = 6{\cdot}9 \pm {\cdot}2$ $\quad \text{Log } A = 11{\cdot}8 \pm {\cdot}1$

FIG. 11.

HYDROGEN ATOM ABSTRACTION BY $CF_3\cdot$ AND $CH_3\cdot$ FROM TRIMETHYLSILANE AND TETRAMETHYLSILANE



● ABSTRACTION FROM Me_3SiH

Upper Curve: $CF_3\cdot$ Lower Curve: $CH_3\cdot$

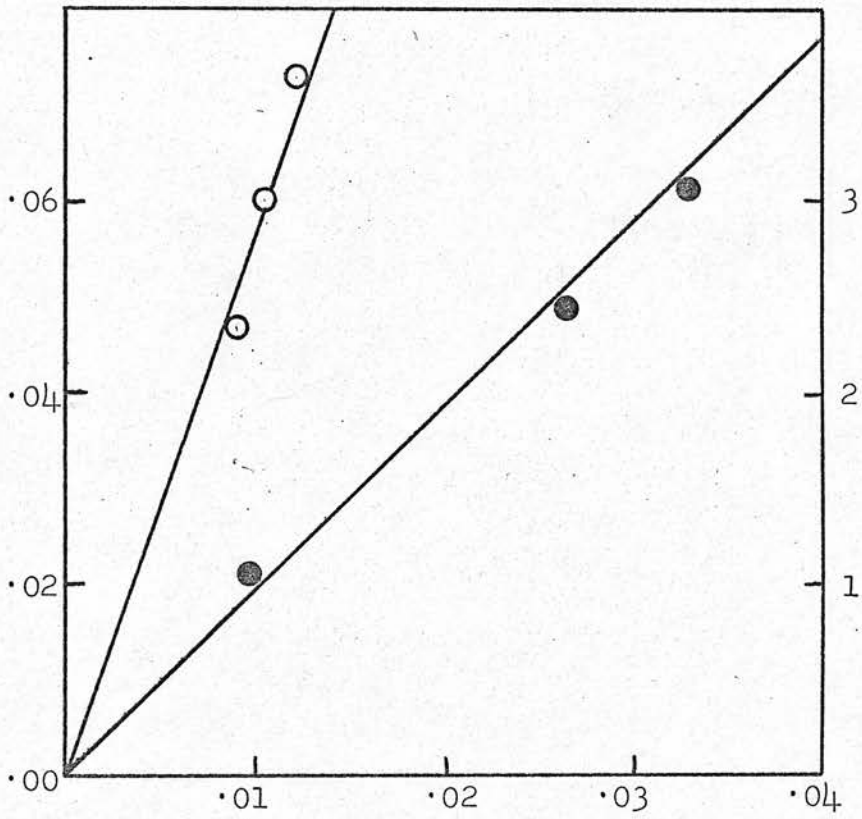
○ ABSTRACTION FROM Me_4Si

Upper Curve: $CF_3\cdot$ Lower Curve: $CH_3\cdot$

FIG.12.

$CF_3\cdot$ AND CH_3 ATTACK ON SILANE

TEST OF MECHANISM



$\frac{10^{-6}}{R^{\frac{1}{2}}_{C_2H_6}}$

$\frac{10^{-6}}{R^{\frac{1}{2}}_{C_2F_6}}$

$10^{-6}[SiH_4]/R_{Rad\ H}$

$SiH_4 + Rad \longrightarrow SiH_3\cdot + RadH$

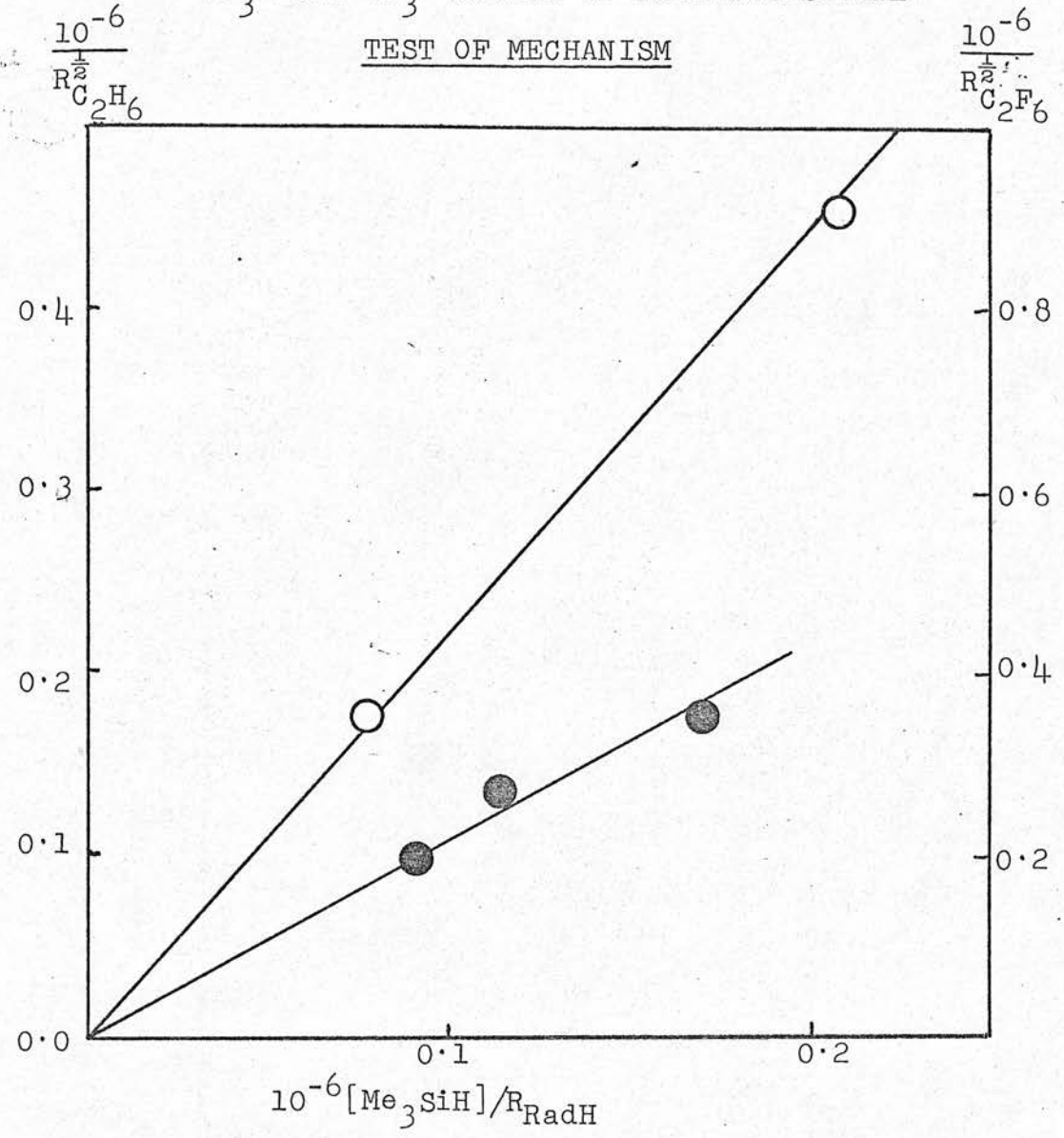
○ Rad = $CF_3\cdot$ at 71·6°C (1000/T = 2·90)

● Rad = $CH_3\cdot$ at 71·6°C

FIG. 13.

$CF_3\cdot$ and $CH_3\cdot$ ATTACK ON TRIMETHYLSILANE

TEST OF MECHANISM



$Me_3SiH + Rad \longrightarrow Me_3Si\cdot + RadH$ Temp. = 97·2

● Rad = $CH_3\cdot$; ○ Rad = $CF_3\cdot$; (1000/T = 2·70)

Allowance is made for the reaction:

$Rad\cdot + (CH_3)_3SiH \longrightarrow (CH_3)_2SiHCH_2\cdot + RadH$ (k_{TRI})

by assuming $k_{TRI}=k_{TETRA}$.

$Rad\cdot + (CH_3)_4Si \longrightarrow (CH_3)_3SiCH_2\cdot + RadH$ (k_{TETRA})

PHOTOLYSIS OF TFMI IN THE PRESENCE OF TETRAMETHYLSILANE.

$$(CH_3)_4Si + CF_3\cdot \longrightarrow (CH_3)_3SiCH_2\cdot + CF_3H$$

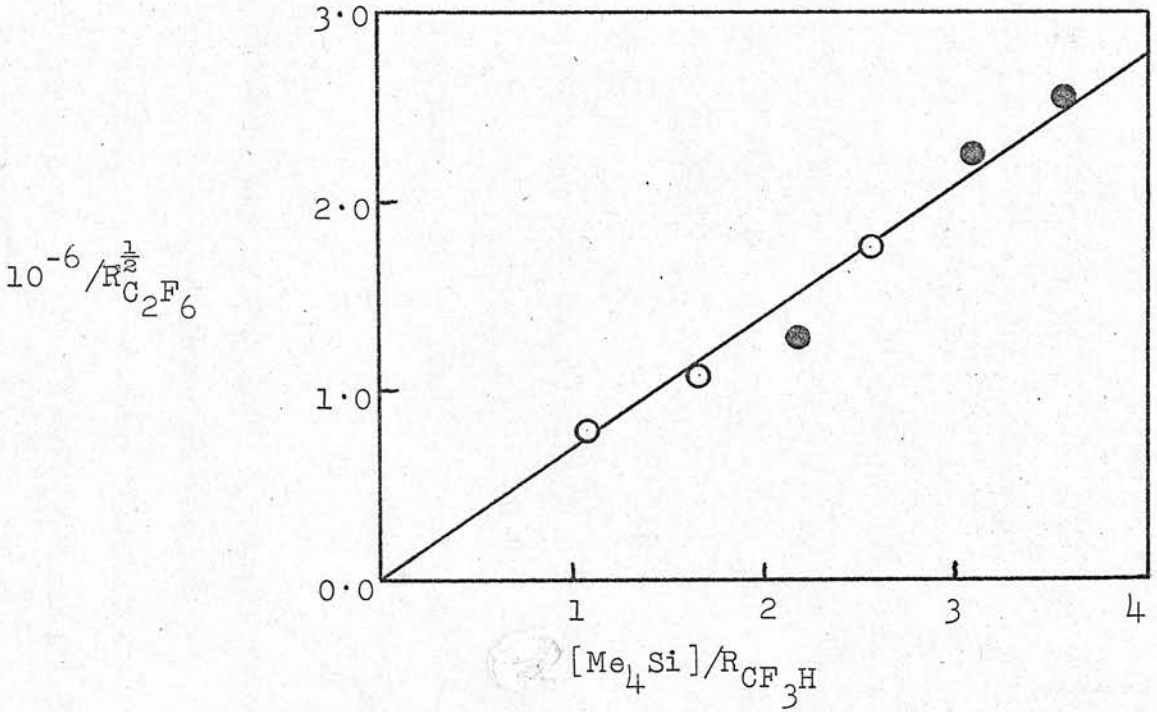


FIG. 14.

TEST OF MECHANISM

The co-incidence of the two sets of points arises from the fact that:

$\bar{R}_{203} \approx 10 \times \bar{R}_{97}$

○ At 97·2°C: $[Me_4Si]/R_{CF_3H}$ is in 10^5 secs.

● At 203°C: " " " " 10^4 "

The results of Kerr and his co-workers (98) for abstraction from Me_4Si by both $CH_3\cdot$ and $CF_3\cdot$ are in excellent agreement with those obtained in the present work, and within experimental error are identical with those reported for neopentane. i.e.

$CH_3 + M(CH_3)_4 \longrightarrow CH_4 + M(CH_3)_3CH_2\cdot$ $E = 10\cdot2 \pm \cdot2$kcal/mole; Log A = $11\cdot5 \pm \cdot2$

$CF_3 + M(CH_3)_4 \longrightarrow CF_3H + M(CH_3)_3CH_2\cdot$ $E = 7\cdot4 \pm \cdot2$kcal/mole; Log A = $11\cdot9 \pm \cdot1$

(M ≡ C or Si)

The difference of around 2·8 kcal in the activation energy requirements for $CH_3\cdot$ and $CF_3\cdot$ is in accord with that reported for hydrocarbon systems (77). It is evident that the substitution of silicon for carbon as central atom has little effect on the kinetics of abstraction from the methyl groups. This is in disagreement with the findings of Chaudry and Gowenlock (104) who observed a marked lowering in both E and A for abstraction of hydrogen by $CH_3\cdot$ on going from Me_4Si to Me_4Pb. The parameters reported by these workers for tetramethylsilane differ from those obtained in the present work, and by Kerr and his co-workers, by an amount considerably outwith experimental error. The reason for this discrepancy is not clear.

Arrhenius parameters for abstraction reactions in which a silicon-hydrogen bond is severed are recorded in Table 23, along with parameters for abstraction from the corresponding alkane. The kinetic data for methyl radical attack on trimethylsilane are in reasonable accord with those of Kerr, Slater and Young (99).

TABLE 22

Hydrogen Abstraction from Group IV Tetramethyls

	E	Log A	Log k_{164}	Ref.
$CH_3\cdot$ + Me_4C	10·0	11·3	6·3	105
$CH_3\cdot$ + Me_4Si	10·3	11·5	6·4	This work
	10·2	11·6	6·4	102
	11·0	12·6	7·1	104
$CH_3\cdot$ + Me_4Ge	9·6	11·8	7·0	"
$CH_3\cdot$ + Me_4Sn	8·6	11·1	6·8	"
$CH_3\cdot$ + Me_4Pb	7·4	10·2	6·5	"
$CF_3\cdot$ + Me_4C	7·6	11·8	8·0	60
$CF_3\cdot$ + Me_4Si	7·6	12·0	8·2	This work
	7·2	11·9	8·3	98

TABLE 23

	Methyl Radicals				Trifluoromethyl Radicals			
	E	Log A	Log k_{164}	Ref.	E	Log A	Log k_{164}	Ref.
SiH_4	6·9	11·8	8·3	p	5·1	11·9	9·3	p
CH_4	14·5	11·8	4·5	a	11·3	12·0	6·3	11
Me_3SiH	7·8	11·3	7·4	p	5·6	12·3	9·5	p
Me_3CH	8·5	11·5	7·2	b	5·3	11·3	8·6	c

a: Mean of parameters from ref. 72.

b: From ref. 111, assuming zero-point energy difference of 1·2 kcal/mole.

c: From ref. 110, results assumed to be internally consistent, but brought into line with n-C_4H_{10} results in chapter 3.

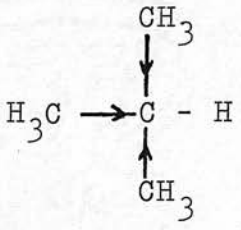
p: This work.

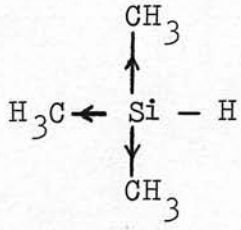
E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$.

For both silane and trimethylsilane the activation energy for abstraction by $CF_3\cdot$ is around 2 kcal/mole lower than that for $CH_3\cdot$. The activation energy for abstraction of hydrogen from methane is around 7 kcal/mole higher than that for silane, with both radicals, while there is little difference in the activation energy requirements for abstraction from Me_3CH and $Me_3Si\,H$. With both radicals the activation energy requirement for abstraction from H_3C-H is 6·0 kcal/mole higher than that for Me_3C-H, while the activation energy for abstraction from H_3Si-H is about 0·6 kcal/mole lower than that for Me_3Si-H for both radicals. In hydrocarbons the labile nature of tertiary hydrogen atoms may be interpreted in terms of bond polarisation leading to enhanced reactivity of the tertiary C-H bond. When silicon is substituted for carbon as the central atom, the situation is reversed, and the Si-H bond is stabilised by electron withdrawal.

Pauling Electronegativities

H : 2·1
C : 2·5
Si : 1·8





The Si-H bond strength in trimethylsilane is not known with any certainty, values reported for $D(Me_3Si\text{-}H)$ ranging from 64 to 88 kcal/mole (105, 106, 107)

The data recorded in Table 23 provide an excellent illustration of the effect of dipolar interactions in radical-molecule reactions.

For attack on the non-polar molecules CH_4 and SiH_4 by either radical, a value of 11·9 ± ·1 is obtained for Log A. On a per-hydrogen atom basis this corresponds to 11·3, in excellent agreement with the observed A-factors for abstraction of the single tertiary hydrogen atom from the essentially non-polar isobutane molecule by either radical and from Me_3SiH by the essentially non-polar methyl radical. The A-factor for attack of the highly polar $CF_3\cdot$ radical on the polar trimethylsilane molecule however, is 10 times greater.

$$\overset{\delta+\ \ \delta-}{Me_3Si - H} \qquad \overset{\delta+\ \delta-}{CF_3\cdot}$$

This may be interpreted in terms of electrostatic attraction between the negatively charged hydrogen atom and the positively charged attacking radical. While the forces involved will be small by comparison with the total kinetic energy of the system, leaving the activation energy unaffected, the relatively long-range nature of such attractions may substantially increase the number of effective collisions, due to "harpooning," with consequent increase in the observed A-factor. If this interpretation is valid we should expect low A-factors for attack of $CF_3\cdot$ radicals on hydrogen atoms bonded to atoms of high electronegativity.

e.g. $\overset{\delta-\ \ \delta+}{MeO - H}$ $\overset{\delta+\delta-}{CF_3}$ $\qquad$ $\overset{\delta-\ \ \delta+}{MeNH - H}$ $\overset{\delta+\delta-}{CF_3}$

This is, in fact, found to be the case, as will be seen in later chapters.

CHAPTER 5

In view of the high electronegativity of oxygen, the abstraction of hydrogen from alcohols by polar radicals should involve considerable dipole-dipole interaction. To investigate this, trifluoromethyl radicals, generated by the photolysis of CF_3I, have been reacted with methanol and trideuteromethanol. The results obtained are given in Tables 24 to 26 and presented graphically in Figs. 15 to 18. When this work began, conflicting values had been reported for the Arrhenius parameters of the corresponding methyl radical reactions.

TABLE 27.

	Shannon and Harrison(117)			Shaw and Thynne (80)		
	E	Log A	Log k_{164}	E	Log A	Log k_{164}
$C\underline{D}_3OH$	11·7	11·3	5·4	9·3	10·2	5·5
$C\underline{H}_3OH$	10·4	11·4	6·2	8·1	10·4	6·3
$CD_3O\underline{H}$	6·4	9·3	6·1	9·0	10·5	6·0

The hydrogen abstracted is underlined.

Recently (113) Gray has attributed this discrepancy to a heterogenous hydrogen exchange reaction between the hydroxyl group of the alcohol and the methyl groups of the radical source, acetone having been used by Shannon and Harrison, and hexadeuteroacetone by Shaw and Thynne. In order to overcome this difficulty Gray and Herod (114) have repeated the investigation using compatibly labelled methanol and acetone, i.e. CD_3COCD_3 with CD_3OD, and CH_3COCH_3 with CH_3OH and CD_3OH. The results are shown in Table 28, together with the corresponding parameters for abstraction by trifluoromethyl radicals.

TABLE 24

Photolysis of TFMI in the Presence of Trideuteromethanol

RUN	T(°K)	t(sec)	CD_3OH	CF_3I	CF_3H	CF_3D	C_2F_6	R_H	R_D	1000/T	Log R_H	Log R_D
148	357·1	1200	·395	1·59	1·72	·077	·877	4·64	·210	2·80	0·666	$\bar{1}$·322
155	357·1	1500	·291	1·57	1·69	·076	·711	6·88	·311	2·80	0·837	$\bar{1}$·493
153	357·1	1800	·249	1·76	1·62	·073	·650	8·08	·366	2·80	0·907	$\bar{1}$·563
152	370·2	1200	·182	1·29	1·35	·071	·730	8·66	·458	2·70	0·937	$\bar{1}$·661
154	384·5	1800	·278	1·50	1·72	·109	·617	7·88	·497	2·60	0·897	$\bar{1}$·697
147	384·6	2400	·210	1·45	1·73	·019	·458	12·2	·769	2·60	1·086	$\bar{1}$·886
151	400·0	1800	·202	1·43	1·67	·125	·638	10·3	·772	2·50	1·014	$\bar{1}$·887
149	400·0	2500	·335	1·35	2·24	·168	·356	11·2	·838	2·50	1·050	$\bar{1}$·923
85	416·6	1800	·348	·788	2·25	·199	·357	10·8	·959	2·40	1·034	$\bar{1}$·982
150	416·8	1800	·237	·953	2·28	·202	·483	15·5	1·38	2·40	1·192	0·140
145	434·8	450	·222	1·54	3·61	·382	1·64	12·7	1·34	2·30	1·102	0·127
146	434·8	2000	·213	1·47	2·45	·259	·471	16·7	1·77	2·30	1·224	0·248

CD_3OH and CF_3I are in 10^{-6} mole cm^{-3}; CF_3H, CF_3D and C_2F_6 in 10^{-12} mole $cm^{-3} sec^{-1}$

R_H refers to abstraction from the OH group, R_D to abstraction from CD_3.

TABLE 25

Photolysis of TFMI in the Presence of Methanol

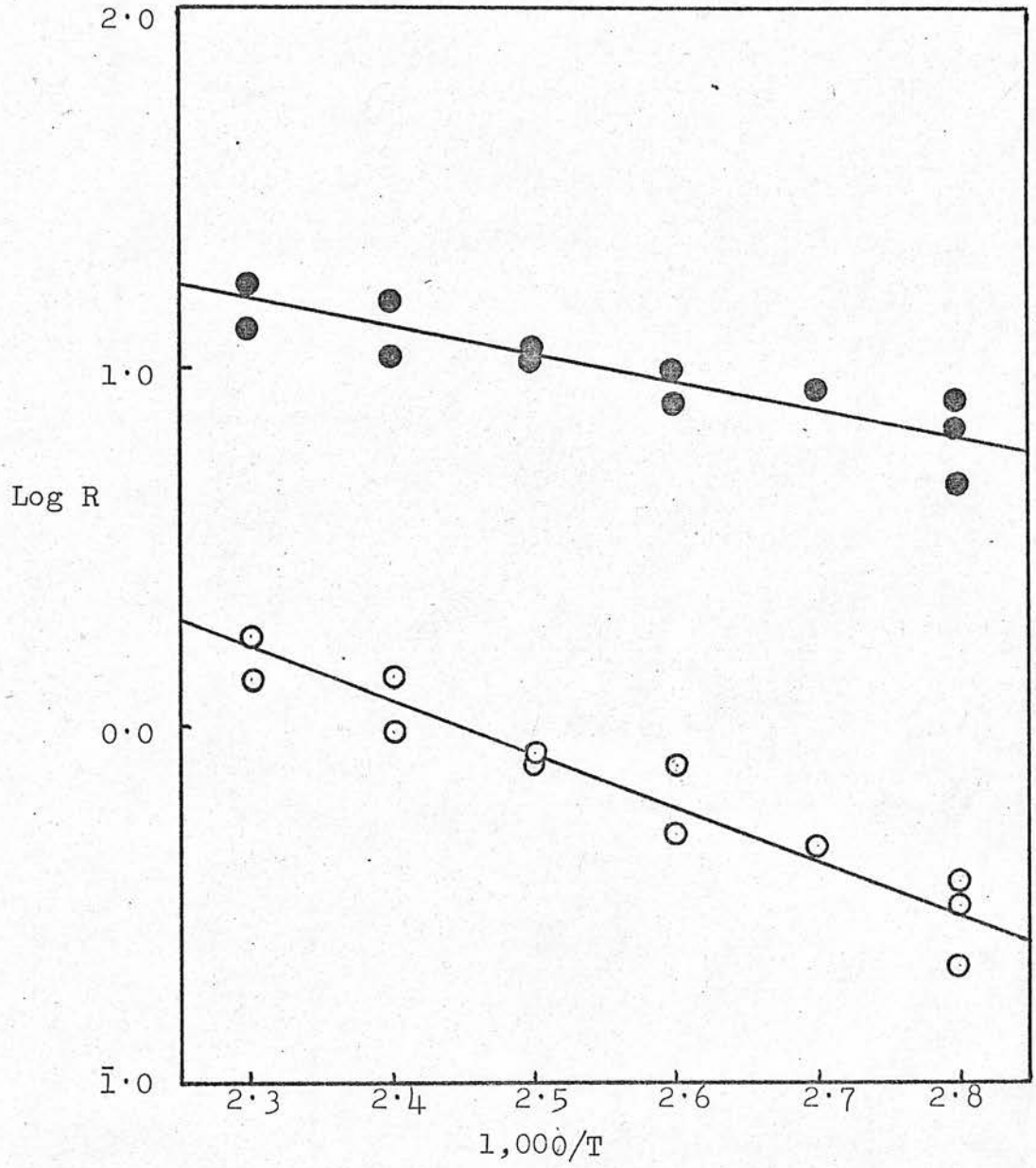
RUN	T(°K)	t(sec)	MeOH	TFMI	CF_3H	C_2H_6	R	1000/T	$Log_{10}R$
43	356·8	1200	·496	1·38	3·69	·734	8·7	2·80	0·940
45	357·0	1200	·285	1·66	2·36	·867	8·9	2·80	0·949
42	357·1	1800	·369	1·49	2·49	·555	9·0	2·80	0·954
38	370·2	1800	·193	1·72	1·90	·723	11·6	2·70	1·065
39	370·2	1800	·570	1·75	3·93	·500	9·7	2·70	0·987
41	384·5	1200	·363	1·47	3·72	·689	12·3	2·60	1·090
37	384·9	1200	·195	1·74	2·77	·920	14·8	2·60	1·170
36	400·0	600	·593	1·23	7·29	·734	14·3	2·50	1·155
35	400·1	1200	·619	1·29	6·51	·520	14·6	2·50	1·164
34	400·3	1200	·247	1·68	3·63	·937	15·2	2·50	1·182
30	415·6	900	·236	1·58	5·38	1·13	21·5	2·40	1·332
29	415·6	1800	·240	1·60	4·67	·792	21·9	2·40	1·340
20	416·2	200	·230	0·99	6·95	3·51	16·1	2·40	1·207
28	416·4	600	·381	1·03	6·32	·937	17·1	2·40	1·233
22	416·6	600	·334	1·03	7·47	1·00	22·3	2·40	1·348
23	416·6	600	·340	1·04	7·20	·826	23·3	2·40	1·367
31	434·1	240	·386	1·07	11·7	1·81	22·7	2·30	1·356
32	435·0	600	·397	1·10	9·31	·848	25·1	2·30	1·400
33	435·0	600	·229	1·56	6·01	1·09	25·1	2·30	1·400

MeOH and TFMI are in 10^{-6} mole cm^{-3};

CF_3H and C_2F_6 in 10^{-12} mole $cm^{-3}sec^{-1}$.

FIG. 15.

PHOTOLYSIS OF TFMI IN THE PRESENCE OF TRIDEUTEROMETHANOL



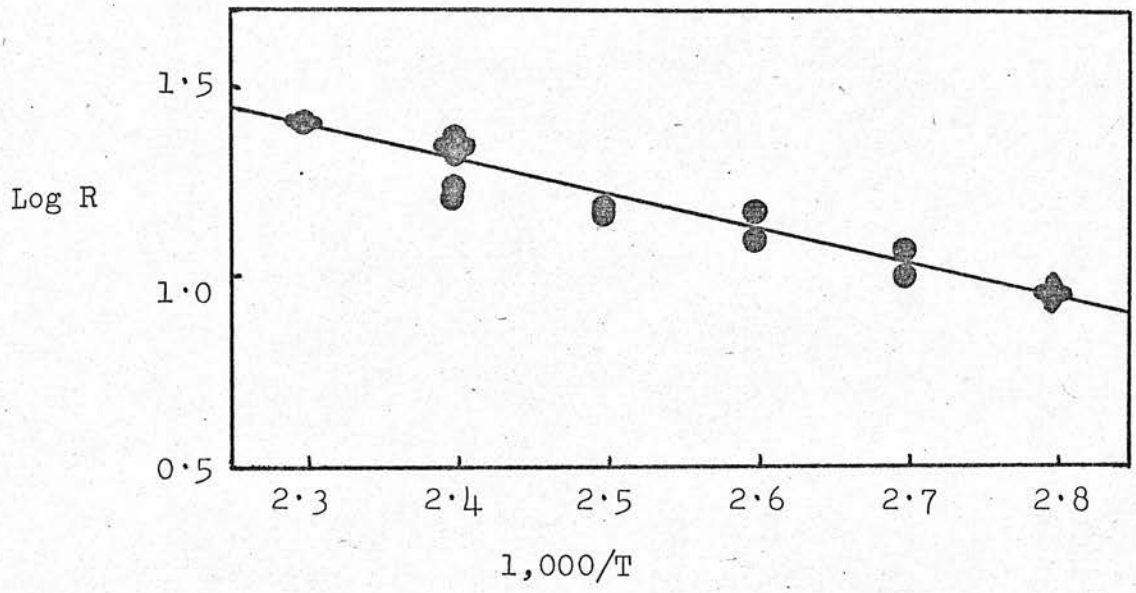
● $CD_3OH + CF_3\cdot \longrightarrow CD_3O\cdot + CF_3H$

○ $CD_3OH + CF_3\cdot \longrightarrow \cdot CD_2OH + CF_3D$

PHOTOLYSIS OF TFMI IN THE PRESENCE OF METHANOL

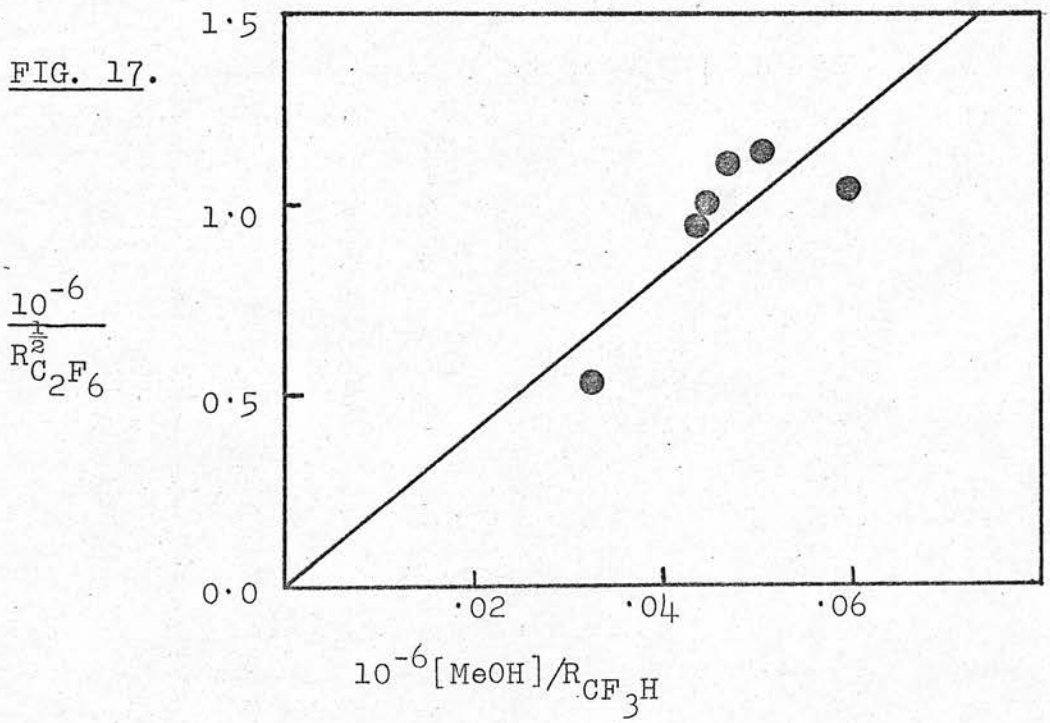
OVERALL ABSTRACTION OF HYDROGEN

FIG. 16.



TEST OF MECHANISM

FIG. 17.



HYDROGEN AND DEUTERIUM ATOM ABSTRACTION FROM CD_3OH

TABLE 26. - Relative Rates of Attack.

Temp. (°C)	161·6	143·4	126·8	111·4	97·2	83·9
1000/T	2·3	2·4	2·5	2·6	2·7	2·8
% CF_3D (By mass-spec.)	8·94	9·07	6·63	7·93	5·20	3·93
	10·61	9·38	6·43	6·02	5·47	4·37
	9·29	7·73	6·87	4·27	5·63	5·14
	7·47	7·81	6·11	8·03	4·66	5·14
				4·78	5·14	3·65
					4·09	3·73
MEAN:	9·08	8·50	6·51	6·21	5·03	4·33
Log_{10}MEAN	0·96	0·93	0·81	0·79	0·70	0·64

The Temperature Dependence of the Relative Rates of Attack is shown in Fig. 18 below.

FIG.18

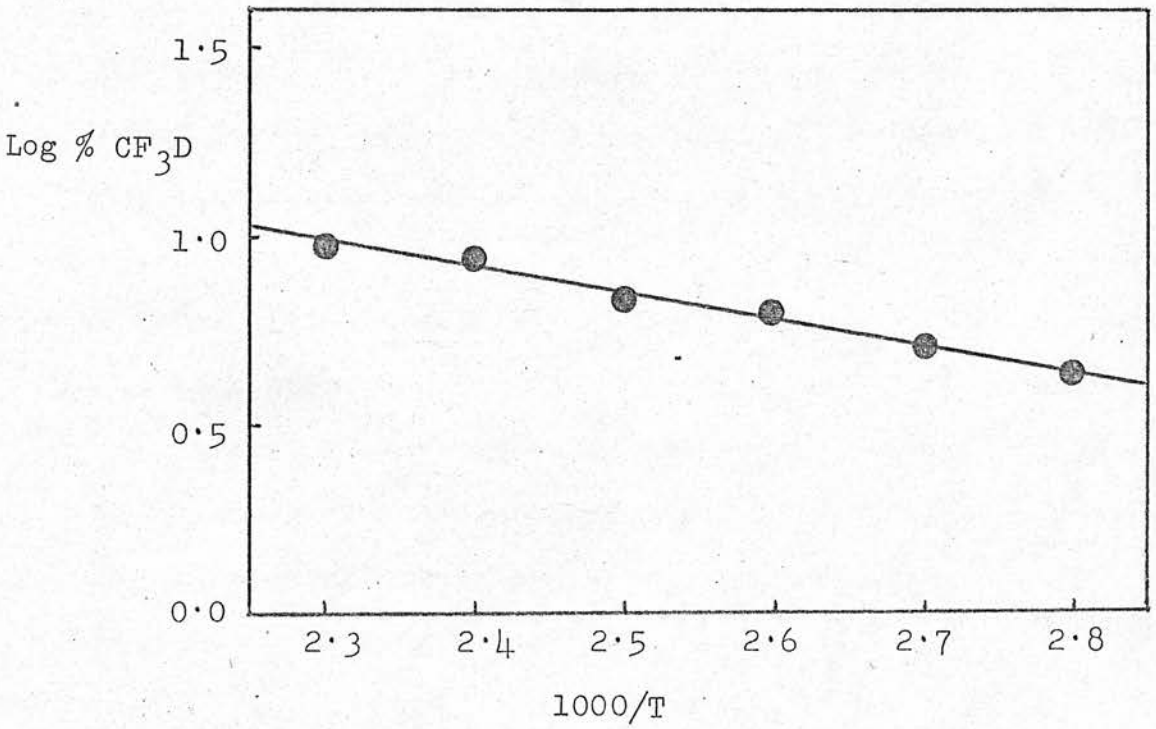


TABLE 28

	Methyl (114)			Trifluoromethyl (This work)		
	E	Log A	Log k_{164}	E	Log A	Log k_{164}
$CD_3\underline{H}$	11·9	11·3	5·3	6·6	10·2	6·9
$C\underline{H}_3OH$	10·0	11·3	6·3	4·7	10·0	7·6
$CD_3\underline{O}H$	9·5	10·5	5·7	3·2	9·5	7·9
$E_D - E_H$	1·9 kcal/mole			1·9 kcal/mole		

The hydrogen abstracted is underlined.

E is in kcal/mole. A and k_{164} in $mole^{-1}cm^3sec^{-1}$.

With both radicals, the activation energy for abstraction from the hydroxyl group is lower than that for the methyl group, the difference being around 1 kcal/mole. At high temperatures, however, abstraction from the methyl position is favoured, the A-factor being about ten times greater. Methanol is considerably more reactive with $CF_3\cdot$ than with $CH_3\cdot$, by a factor of about 50 at 164°C, due to the marked lowering in activation energy requirements with the polar radical, the difference being around 6 kcal/mole for both positions. This is considerably in excess of the differences found for non-polar molecules, and may be compared with the low values obtained for silanes, where the polarity is reversed.

The activation energy for abstraction of hydrogen from the alkyl position by either radical is 1·9 kcal/mole lower than that for abstraction of deuterium. Since the zero-point energy difference corresponding to a single C-H and C-D stretching vibration is 1·2 kcal/mole the possibility of tunnelling cannot be ruled out.

As predicted in the previous chapter, the A-factor for abstraction from the hydroxyl group by $CF_3\cdot$ is lower than that for $CH_3\cdot$ (by a factor of ten), and is attributed to electrostatic repulsion between the molecule and the incoming radical. A similar lowering is observed for the methyl group. This is discussed more fully in Chapter 8, where Arrhenius parameters are compared for hydrogen abstraction from methyl groups in different chemical environments.

Results obtained by Carlton and his co-workers (70) for the abstraction of hydrogen from methanol by trifluoromethyl radicals differ markedly from those obtained in the present work. These investigators used hexafluoroazomethane as radical source. Due to rapid addition to the azo linkage the radical concentration obtained is low, and the C_2F_6 formed could not be measured accurately. Accordingly, a competitive technique was adopted, using

$$CF_3\cdot + CH_4 \longrightarrow CF_3H + CH_3\cdot$$

as reference reaction. The following parameters were obtained:-

	E	Log A	Log k_{164}
$CF_3 + CH_3OH \longrightarrow CF_3H + \cdot CH_2OH$	8·3	12·2	8·0
$\longrightarrow CF_3H + CH_3O\cdot$	8·3	11·2	7·0

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$.

The overall rate constant for abstraction from CH_3OH at 164^oC is in reasonable agreement with that obtained in the present work. Observed relative rates of attack on

CD_3OH, however, differ radically. For example, at 380°K Carlton reports a ratio of 1·08, as opposed to 0·060. (Fig. 18).

It is suggested that this may be due to disproportation of the trideuteromethoxy radical with $CF_3\cdot$.

$$CF_3\cdot + CD_3OH \longrightarrow CF_3H + CD_3O\cdot$$

$$CD_3O\cdot + CF_3\cdot \longrightarrow D\cdot COD + CF_3D$$

$$CF_3\cdot + CD_3OH \longrightarrow CF_3D + \cdot CD_2OH$$

$$D\cdot COD + CF_3\cdot \longrightarrow CDO\cdot + CF_3D$$

$$CDO\cdot + CF_3\cdot \longrightarrow CO + CF_3D$$

As detailed in Chapter 3, when CF_3I is used as radical source, the presence in the system of high concentrations of iodine atoms, in equilibrium with molecular iodine, appears to inhibit secondary reactions.

In the course of this work an attempt was also made to investigate the kinetics of hydrogen atom abstraction from methyl mercaptan by trifluoromethyl radicals, the corresponding methyl radical reactions having been studied previously by Greig and Thynne (115) whose results are recorded below:-

	E	Log A	Log k_{164}
$CH_3\cdot + CD_3SH \longrightarrow CH_4 + CD_3S\cdot$	4·1	11·0	8·9
$\longrightarrow CH_3D + CD_2SH$	8·3	10·9	6·7

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$.

It was evident from preliminary runs, however, that the rate of abstraction by $CF_3\cdot$ was so great that the yield of C_2F_6 could not be measured with any degree of accuracy. By comparison of the relative rates of formation of CF_3H and C_2F_6 with those for runs performed under similar conditions using trimethylamine, the most labile hydrogen substrate fully investigated (Chapter 6), an estimate of R at 40°C was obtained. For trimethylamine, $R_{40} = 110$; the value for methyl mercaptan is about twenty times greater, thus

$$R_{40}(CH_3SH) \approx 2000 \qquad \therefore \text{ Log } R \approx 3{\cdot}2$$

$$\therefore \underline{\text{Log } k \approx 10{\cdot}0} \text{ at } 40^\circ C.$$

Preliminary investigation of the photolysis of HFA in the presence of dimethylsulphide suggests that in the case of abstraction from CH_3SH less than 1% of the fluoroform results from abstraction from the methyl group. This is in accord with the work of Greig and Thynne for methyl radical attack on CD_3SH.

Since the Pauling electronegativity for sulphur is the same as that for carbon, we would not expect to find the A-factor depression observed for methanol. Taking the value of Log A = 11·3 found for abstraction from a non-polar site (Chapter 4) in conjunction with the estimated value of Log k_{40} = 10, gives an activation energy of about 2 kcal/mole for abstraction from the thiol group by $CF_3\cdot$. In Table 29 these estimated Arrhenius parameters are compared with parameters reported for related abstractions.

TABLE 29.

	METHYL RADICALS				TRIFLUOROMETHYL RADICALS			
	E	Log A	Log k_{164}	Ref.	E	Log A	Log k_{164}	Ref.
H_2S	3·1	11·8	10·2	118	4·1	11·8	9·7	69,116
					1·2	11·2	10·6	71
$CD_3S\underline{H}$	4·1	11·0	8·9	115	1·9	11·3	10·3	Estimated
$CH_3O\underline{H}$	9·5	10·5	5·7	114	3·2	9·5	7·9	This work

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$.

The hydrogen atom abstracted is underlined

Three sets of Arrhenius parameters have been reported for the reaction:

$$CF_3 + H_2S \longrightarrow CF_3H + SH$$

Two of these were obtained by N.L. Arthur working in different Laboratories (69, 116), the third by Kale and Timmons (71) who report an extremely low activation energy, but normal A-factor. The difference between these determinations results from a ten-fold discrepancy in observed rate constants, and cannot be explained in terms of compensation of Arrhenius parameters. The high reactivity of methyl mercaptan towards $CF_3\cdot$ attack appears to lend support to the higher values reported by Kale and Timmons. On the basis of their work, and the parameters estimated for CH_3SH, the activation energy requirement for hydrogen atom abstraction from S-H by $CH_3\cdot$ is around 2 kcal/mole greater than for $CF_3\cdot$.

Greig and Thynne have reported Arrhenius parameters for the reaction $CH_3\cdot + CD_3SH \longrightarrow CH_3SH + CD_3\cdot$

A similar group abstraction was observed for trifluoromethyl radical attack on methanol.

$$CF_3\cdot + CD_3OH \longrightarrow CF_3OH + CD_3\cdot$$

When CF_3I was photolysed in the presence of CD_3OH, small amounts of products volatile at -196°C were formed. Mass-spectrometric analysis showed these to be CD_3H and CD_4 formed by the following reactions.

$$CD_3\cdot + CD_3OH \longrightarrow CD_4 + \cdot CD_2OH$$

$$\longrightarrow CD_3H + CD_3O\cdot$$

CHAPTER 6

When this work was started, in 1966, no kinetic data had been reported for hydrogen abstraction reactions involving the severing of an N-H bond by $CF_3\cdot$. Accordingly a study was made of the photolysis of CF_3I in the presence of ammonia, all fluoroform and hexafluoroethane being attributed to the following reactions.

$$CF_3I + h\nu \longrightarrow CF_3\cdot + I\cdot$$

$$CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6 \qquad (k_c)$$

$$CF_3\cdot + NH_3 \longrightarrow CF_3H + NH_2\cdot \qquad (k_a)$$

TABLE 30

Photolysis of TFMI in the Presence of Ammonia

RUN	T(°K)	t(sec)	NH_3	CF_3I	CF_3H	C_2F_6	R	1000/T	Log R
229	303·0	450	1·99	1·95	0·90	4·97	0·204	3·30	$\bar{1}$·31
232	322·6	450	2·08	2·04	1·12	4·77	0·247	3·10	$\bar{1}$·39
227	344·8	450	4·86	0·99	3·58	4·31	0·355	2·90	$\bar{1}$·55
230	370·3	450	1·76	1·72	1·89	3·50	0·577	2·70	$\bar{1}$·76
248	384·6	450	2·74	1·50	2·64	1·69	0·741	2·60	$\bar{1}$·87
231	400·0	450	1·53	1·50	3·13	3·56	1·08	2·50	0·03
247	416·6	500	2·56	1·41	4·12	1·13	1·52	2·40	0·18
226	434·8	450	5·85	1·19	22·5	3·25	2·13	2·30	0·33
246	454·5	450	2·53	1·39	6·21	0·63	3·10	2·20	0·49
245	500·0	500	2·38	1·31	12·4	0·25	10·4	2·00	1·02
244	555·5	300	2·62	1·44	62·5	0·24	48·4	1·80	1·68
243	625·2	450	1·78	0·98	480	0·34	461	1·60	2·66

NH_3 and CF_3I are in 10^{-6} moles cm^{-3};
CF_3H and C_2F_6 in 10^{-12} mole $cm^{-3}sec^{-1}$.

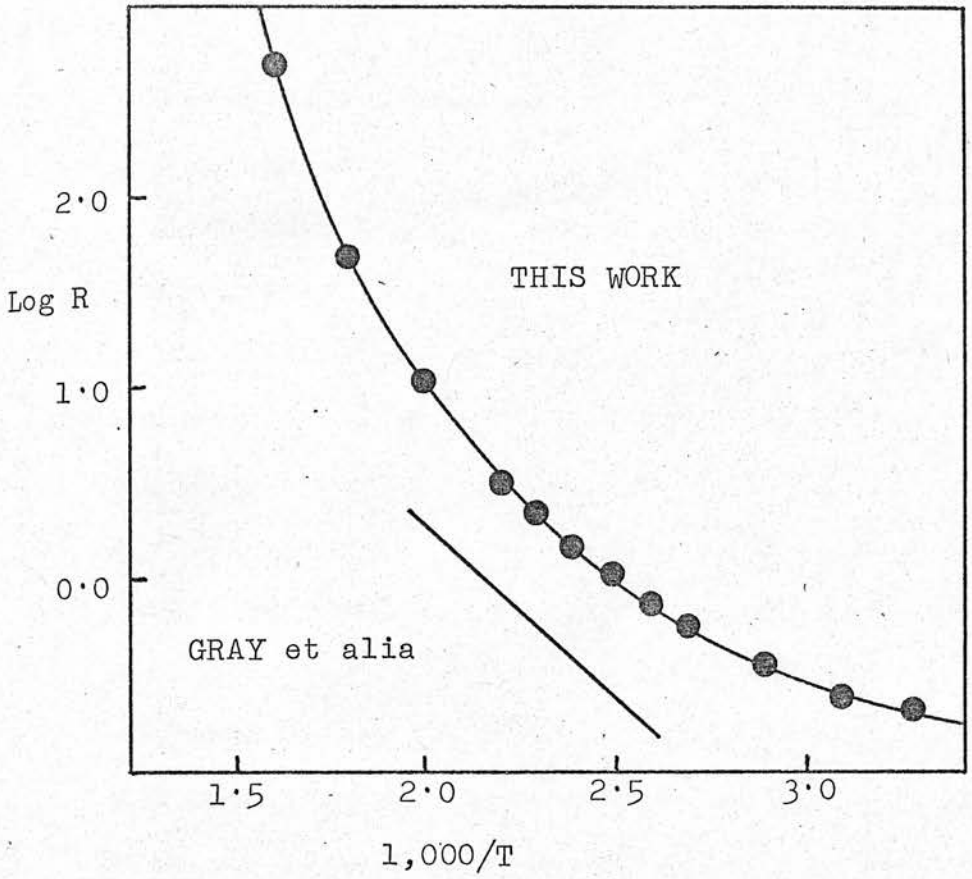
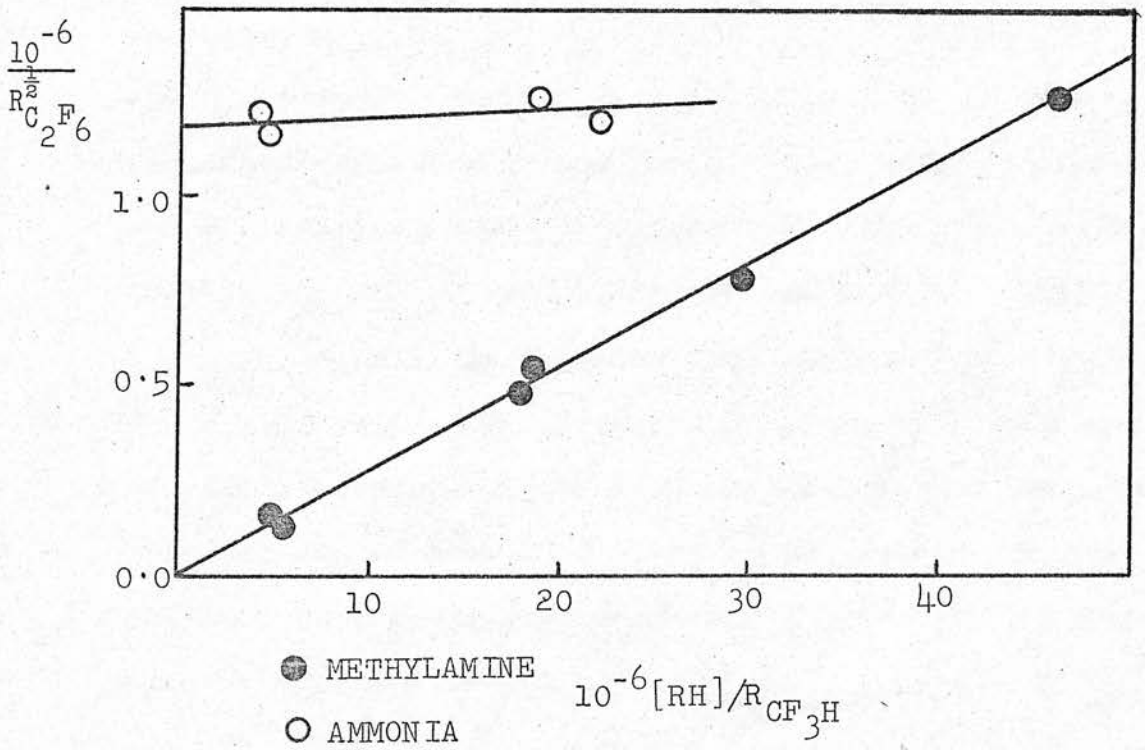


FIG. 19.

CF_3· + AMMONIA

FIG. 20. TEST OF MECHANISM (60°C)



The resulting Arrhenius plot for k_a, however, showed marked curvature (Table 30 and Fig. 19). Since it is evident that the rate of abstraction from ammonia is considerably lower than that for other substrates studied, contamination was immediately suspected. Accordingly a new vacuum system was constructed (a simplified version of the line described in Chapter 2) avoiding the use of hydrocarbon grease. Two different samples of ammonia were used: ICI redistilled ammonia was bulb-to-bulb distilled, a middle fraction being stored at -196°C; a sample prepared by heating an intimate mixture of soda-lime and ammonium chloride was purified by repeated slush-bath distillation: preliminary runs showed the samples to react with $CF_3\cdot$ at identical rates. No systematic variation of R with run time, which would be expected if traces of a highly reactive impurity were being used up preferentially, was observed.

The reaction was then studied at four different temperatures, using a wide range of run times and reactant concentrations: the results are recorded in Table 31. In Fig. 20 $1/R^{\frac{1}{2}}_{C_2F_6}$ at 60°C is plotted against $[NH]/R_{CF_3H}$ A similar plot is shown for CH_3NH_2 (Table 32). It is evident that while for methylamine R is independent of radical concentration, the same is not true for ammonia. Figs. 21 and 22 show similar plots at each of the temperatures studied: while the graphs appear to be linear they do not pass through the origin.

TABLE 31

$CF_3\cdot$ Attack on Ammonia: Clean Vacuum System.

RUN	T(°K)	t(sec)	NH_3	CF_3I	CF_3H	C_2F_6	$\frac{1000}{T}$	$\frac{NH_3}{CF_3H}$	$\frac{1}{C_2F_6}$
348	333·3	3600	1·21	1·21	0·296	0·687	3·00	4·10	1·21
346	333·3	1800	1·11	0·29	0·237	0·762	3·00	4·70	1·15
352	333·3	3600	4·11	0·42	0·217	0·642	3·00	18·9	1·25
366	333·3	3600	2·94	0·70	0·133	0·534	3·00	22·1	1·37
361	370·4	3600	0·91	1·96	0·669	0·700	2·70	1·36	1·20
360	370·4	3600	1·30	1·33	0·546	0·590	2·70	2·37	1·30
367	370·4	3600	2·45	0·59	0·161	0·228	2·70	15·2	2·10
344	434·8	1800	1·40	0·37	0·995	0·742	2·30	1·41	1·16
345	434·8	1800	1·35	0·35	0·914	0·625	2·30	1·47	1·27
355	434·8	1800	2·28	0·23	1·041	0·553	2·30	2·19	1·34
354	434·8	1800	4·71	0·48	0·406	1·061	2·30	3·55	1·78
368	434·8	3600	2·65	0·64	0·698	0·338	2·30	3·80	1·72
369	434·8	7200	1·94	0·47	0·471	0·228	2·30	4·12	2·10
365	500·0	1800	0·52	1·11	1·261	0·755	2·00	0·41	1·15
364	500·0	4200	0·68	1·45	1·137	0·438	2·00	0·60	1·52
358	500·0	6000	1·10	1·13	1·082	0·273	2·00	1·02	1·92
359	500·0	12000	1·43	1·47	1·036	0·165	2·00	1·38	2·47

NH_3 and CF_3I are in 10^{-6} mole cm^{-3};
CF_3H and C_2F_6 in 10^{-12} mole $cm^{-3}sec^{-1}$;
NH_3/CF_3H in 10^6 sec., and $1/(C_2F_6)^{\frac{1}{2}}$ in
10^6 $mole^{-\frac{1}{2}}$ $cm^{\frac{3}{2}}$ $sec^{\frac{1}{2}}$.

PHOTOLYSIS OF TFMI IN THE PRESENCE OF AMMONIA

FIG. 21.

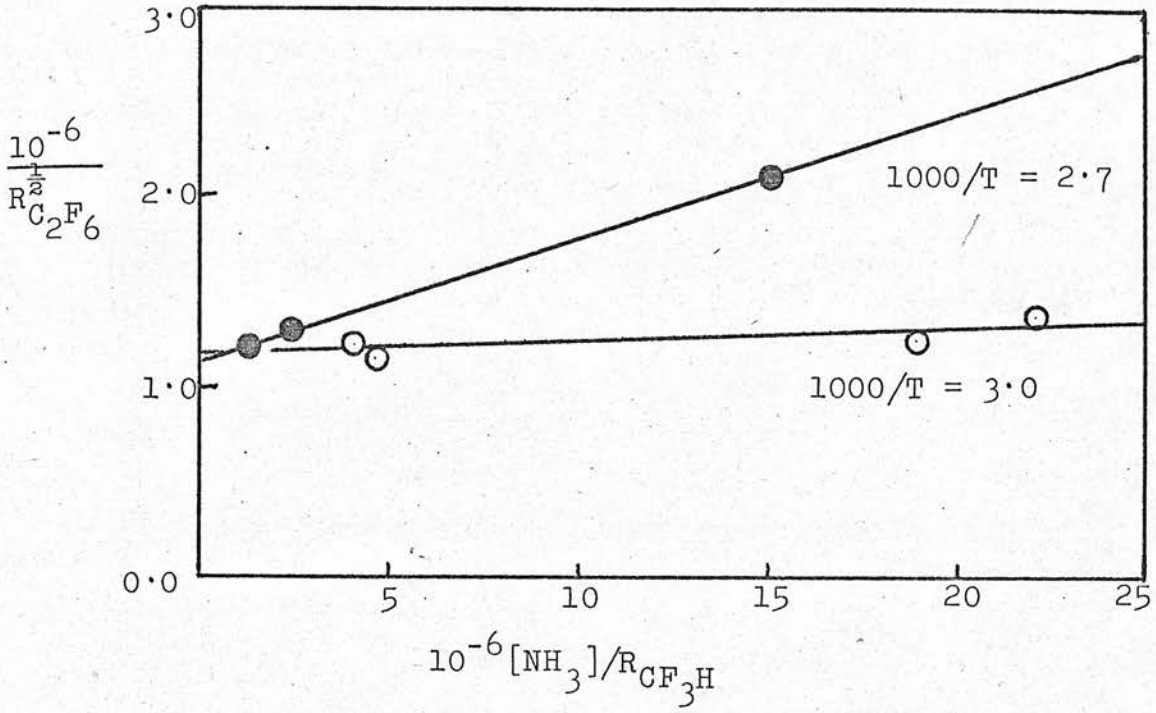
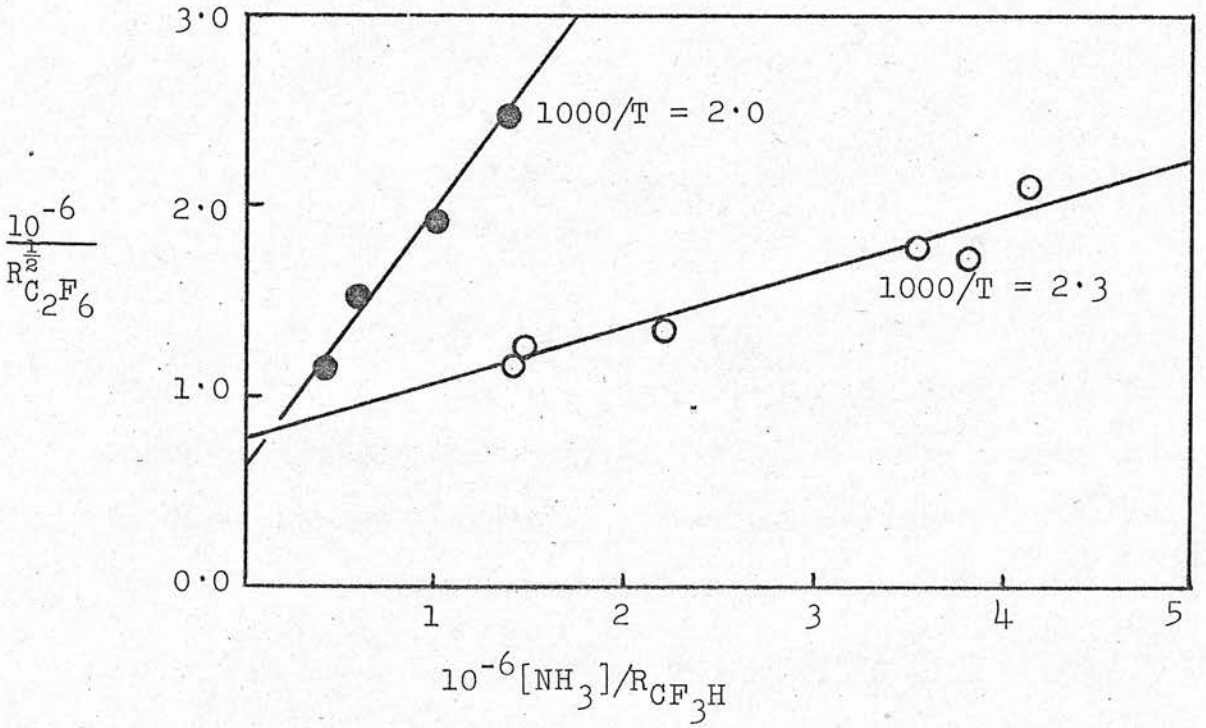


FIG. 22.



While no conclusive explanation of these observations may be advanced, it seems probable that reactions of $NH_2\cdot$ radicals formed by the primary abstraction process will complicate the mechanism. If we suppose these radicals to give rise to some intermediate XH, then additional fluoroform will result from the reaction:-

$$XH + CF_3 \longrightarrow CF_3H + X\cdot \qquad (k_x)$$

Thus

$$R_{CF_3H} = k_a[CF_3][NH_3] + k_x[CF_3][XH] = \frac{R_{C_2F_6}^{\frac{1}{2}}}{k_c^{\frac{1}{2}}} \left\{ k_a[NH_3] + k_x[XH] \right\}$$

If XH arises from $NH_2\cdot$, it seems reasonable to suppose that

$$[XH] \propto R_{NH_2}$$
$$\propto R_{CF_3H} \qquad \text{i.e.} \quad [XH] = cR_{CF_3H}$$

where c is a (temperature dependent) constant.

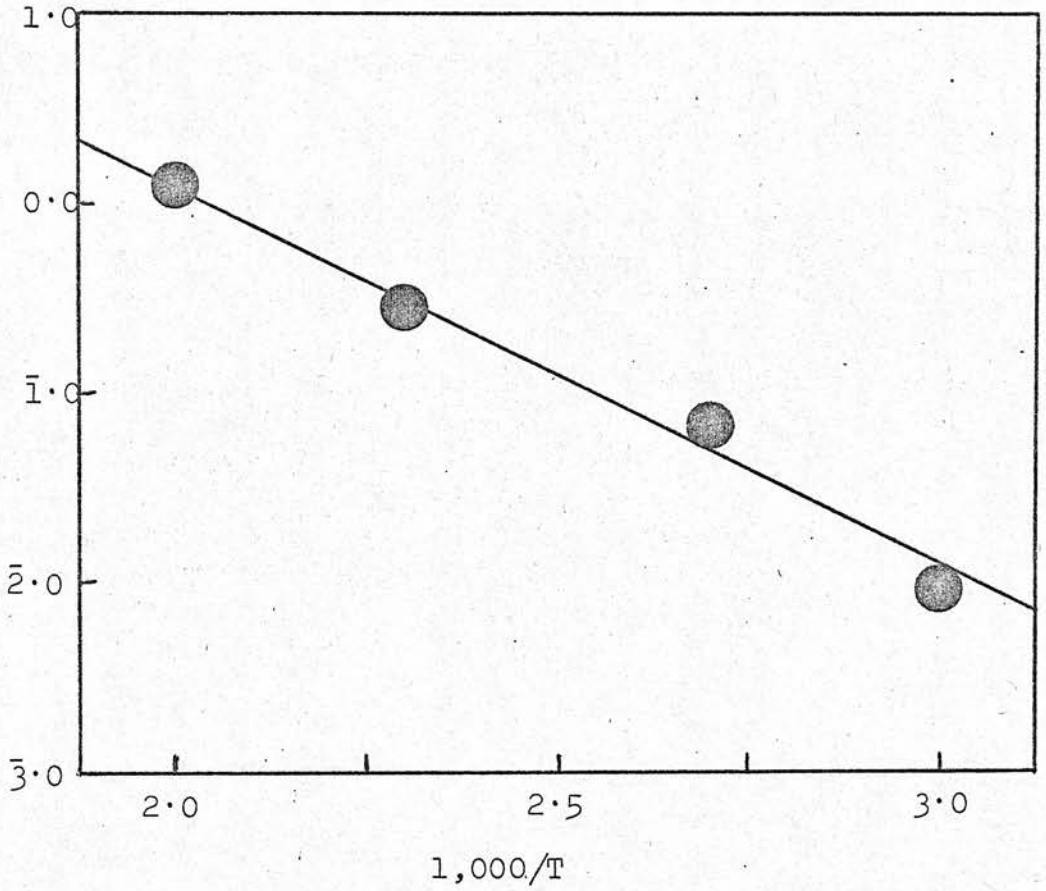
$$\therefore \quad \frac{R_{CF_3H}}{R_{C_2F_6}^{\frac{1}{2}}} = \frac{1}{k_c^{\frac{1}{2}}} \left\{ k_a[NH_3] + ck_xR_{CF_3H} \right\}$$

$$\therefore \quad \frac{1}{R_{C_2F_6}^{\frac{1}{2}}} = \frac{k_a}{k_c^{\frac{1}{2}}} \frac{[NH_3]}{R_{CF_3H}} + ck_x$$

Thus the gradient of a plot of $1/R_{C_2F_6}^{\frac{1}{2}}$ against $[NH]/R_{CF_3H}$ should equal $k_a/k_c^{\frac{1}{2}}$,(R), as in previous systems.
Plotting Log GRADIENT against 1,000/T for the graphs shown in Figs. 21 and 22 gives a linear plot corresponding to the following Arrhenius parameters. (Fig. 23)

$\underline{E = 9 \pm 1}$ kcal/mole $\quad \underline{\text{Log } A = 10{\cdot}8 \pm {\cdot}4}$ $(\text{mole}^{-1}\text{cm}^3\text{sec}^{-1})$

FIG. 23.



This Arrhenius Plot uses the gradients of the plots in Figs. 21 and 22 on P. 112.

In view of the speculative nature of the above treatment it would be unwise to attach any great significance to these parameters. It is evident, however, that the mechanism is considerably more complex than was at first expected. Results reported subsequently by Gray, Arthur and Lloyd (119), using the same radical source, and attributing CF_3H formation solely to the initial abstraction reaction are also indicated in Fig. 19. Over the somewhat narrower temperature range used, the gradient of the Arrhenius plot based on their results corresponds closely to that of the preliminary plot obtained in the present investigation. Unfortunately, the conditions used by these workers did not vary sufficiently to allow the test of mechanism described above to be applied to their data.

Whatever the nature of the complications in the ammonia system, it is clear from Fig. 20 that they do not occur in the case of methylamine, which was also studied in the course of this work. CF_3I was photolysed in the presence of CH_3NH_2, and with CD_3NH_2; the results are recorded in tables 32 and 33 and presented graphically in Figs. 24 and 25. The Arrhenius parameters derived are listed in Table 34 together with those reported by Gray and Thynne (81) for the corresponding reactions of methyl radicals.

The parameters for the NH_2 group are the first to be reported for a reaction in which a hydrogen atom bonded to nitrogen is abstracted by a trifluoromethyl radical.

TABLE 32

Photolysis of TFMI in the Presence of Methylamine.

RUN	T(°K)	t(sec)	$MeNH_2$	CF_3I	CF_3H	C_2F_6	R	$\frac{1000}{T}$	Log R
177	302·9	100	1·21	1·22	90·1	57·7	9·82	3·30	0·994
169	303·1	200	·625	1·86	48·9	69·3	9·40	3·30	0·977
170	312·4	50	·518	1·54	78·3	70·7	18·0	3·20	1·257
178	322·6	100	1·12	1·13	128	48·9	16·3	3·10	1·215
318	333·3	50	·903	·797	50·0	4·64	25·7	3·00	1·411
171	333·3	50	·657	1·95	115	66·8	21·5	3·00	1·333
172	333·3	50	·193	1·97	40·4	45·5	31·0	3·00	1·498
320	333·3	500	·159	1·95	8·47	3·37	29·3	3·00	1·467
317	333·3	500	1·01	·892	33·8	1·86	24·8	3·00	1·394
323	333·3	600	1·48	·559	32·1	·637	27·3	3·00	1·435
179	344·6	150	·845	·849	112	26·8	25·5	2·90	1·411
173	357·1	150	·186	1·90	26·5	18·0	33·5	2·80	1·542
168	370·3	150	·478	1·42	73·8	16·6	37·9	2·70	1·585
174	384·6	50	·174	1·78	44·0	19·4	57·4	2·60	1·761
176	399·8	100	·933	·938	185	8·68	67·2	2·50	1·832
165	416·3	180	·388	1·50	79·7	9·66	66·1	2·40	1·830
166	416·3	100	·348	1·46	93·0	13·1	73·7	2·40	1·875
175	434·8	150	·147	1·50	48·1	9·08	109	2·30	2·044

$MeNH_2$ and CF_3I are in 10^{-6} moles cm^{-3};

CF_3H and C_2F_6 are in 10^{-12} mole $cm^{-3}sec^{-1}$.

TABLE 33

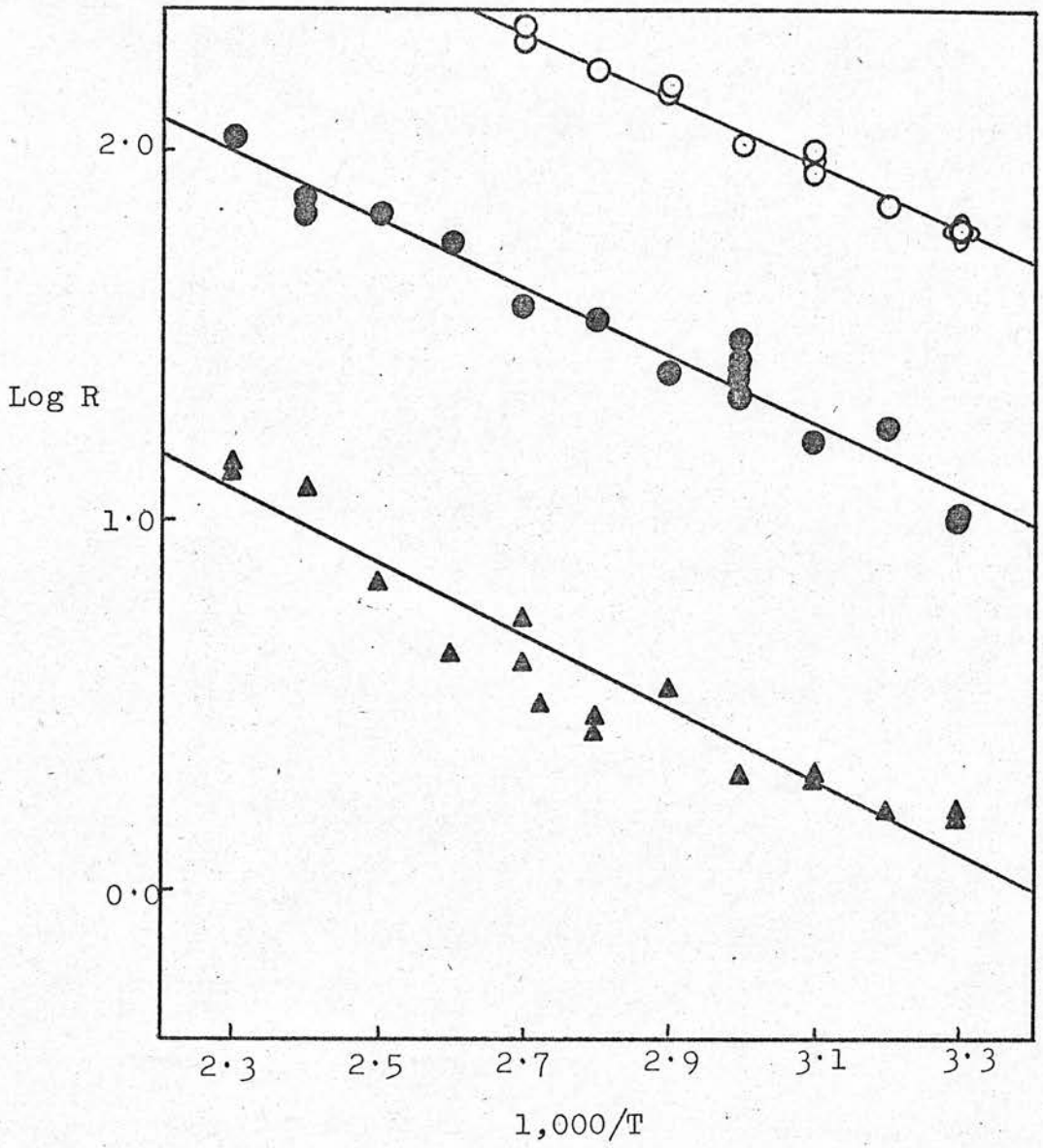
Photolysis of TFMI in the Presence of Trideuteromethylamine

RUN	T(°K)	t(sec)	CD_3NH_2	CF_3I	CF_3H	CF_3D	C_2F_6	R_H	R_D	$\frac{1000}{T}$	Log R_H	Log R_D
183	302·9	250	1·15	1·74	9·82	5·53	29·2	1·59	0·89	3·30	0·200	$\bar{1}$·950
184	303·2	150	1·19	1·25	9·44	6·49	24·0	1·61	1·10	3·30	0·209	0·046
193	312·5	450	0·61	0·68	4·39	3·84	20·5	1·59	1·40	3·20	0·202	0·145
185	322·6	250	0·99	1·04	7·52	7·13	14·3	2·01	1·90	3·10	0·303	0·280
194	333·3	450	0·73	0·75	5·32	6·95	13·3	2·00	2·61	3·00	0·301	0·417
180	344·9	150	0·66	1·00	10·3	10·8	20·9	3·43	3·59	2·90	0·535	0·556
188	357·1	750	0·68	0·94	3·46	5·26	3·66	2·65	4·02	2·80	0·423	0·605
192	357·1	450	0·61	0·68	4·62	6·18	6·77	2·91	3·90	2·80	0·465	0·591
186	370·3	600	0·81	0·85	6·13	8·86	3·57	4·01	5·81	2·70	0·604	0·764
181	370·4	150	0·72	1·09	12·2	15·3	10·1	5·34	6·73	2·70	0·728	0·828
189	384·6	600	0·65	0·89	4·42	7·21	2·44	4·33	7·06	2·60	0·637	0·849
196	400·0	500	0·57	0·59	7·86	13·0	4·03	6·85	11·3	2·50	0·836	1·053
187	416·6	150	0·96	1·01	19·2	25·9	2·89	11·7	15·8	2·40	1·079	1·198
191	434·8	450	0·53	0·60	14·9	22·5	3·71	14·4	21·9	2·30	1·161	1·341
190	434·8	450	0·60	0·82	14·1	23·5	2·95	13·7	22·7	2·30	1·137	1·357

CD_3NH_2 and CF_3I are in 10^{-6} mole cm^{-3}; CF_3H, CF_3D and C_2F_6 are in 10^{-12} mole $cm^{-3}sec^{-1}$.

HYDROGEN ABSTRACTION FROM AMINES BY $CF_3\cdot$

FIG. 24.



○ Overall Abstraction from $(CH_3)_2NH$ by $CF_3\cdot$

● " " - " CH_3NH_2 " "

▲ $CF_3\cdot + CD_3NH_2 \longrightarrow CF_3H + CD_3NH\cdot$

FIG. 25. $CD_3NH_2 + CF_3\cdot \longrightarrow \cdot CD_2NH_2 + CF_3D$

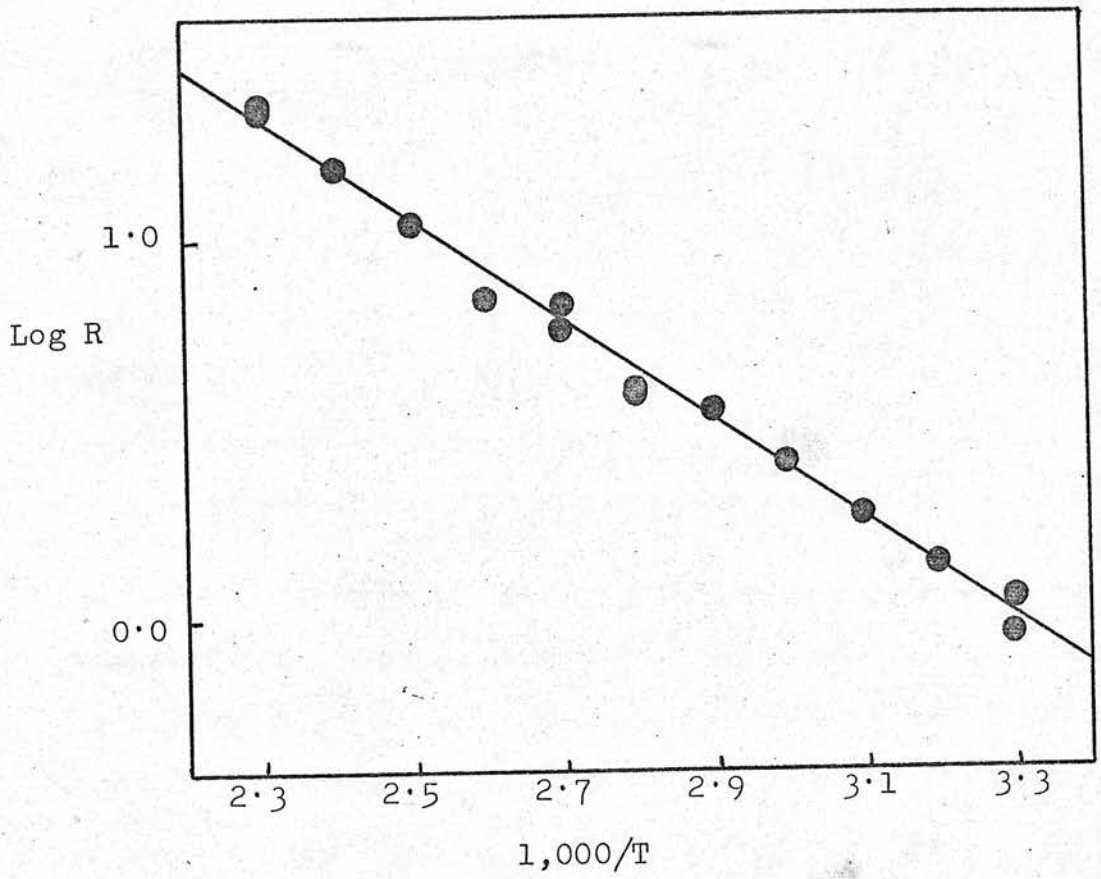
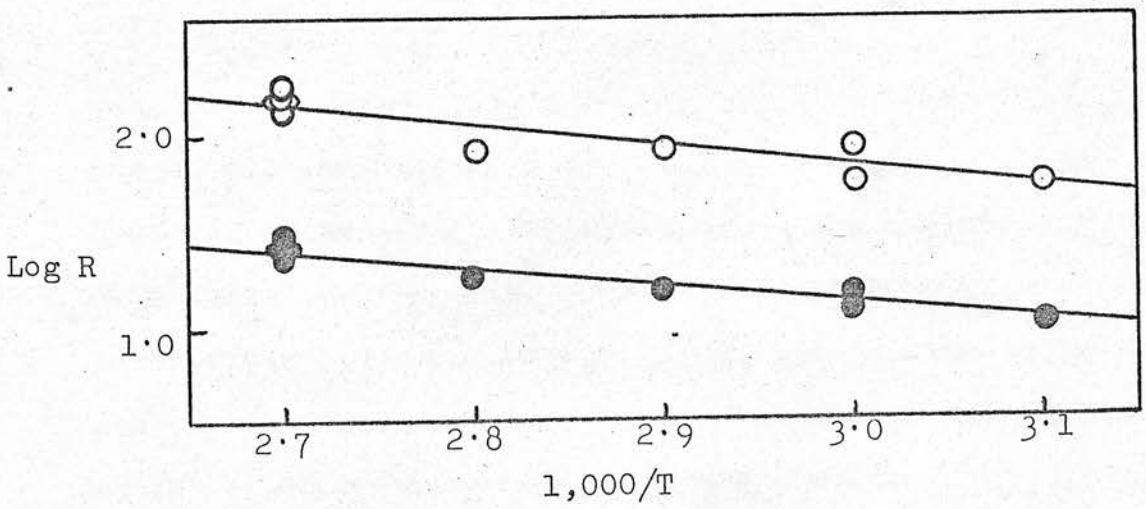


FIG. 26.



○ $(CH_3)_2ND + CF_3\cdot \longrightarrow (CH_3)NDCH_2\cdot + CF_3H$

● $(CH_3)_2ND + CF_3\cdot \longrightarrow (CH_3)_2N\cdot + CF_3D$

TABLE 34

	METHYL RADICALS			TRIFLUOROMETHYL RADICALS			ΔE
	E	Log A	Log k_{164}	E	Log A	Log k_{164}	
$CD_3\underline{NH_2}$	10·1	10·9	5·8	6·1	11·0	7·9	4·0
$CH_3\underline{NH_2}$	8·7	11·0	6·6	4·2	10·7	8·6	4·5
$CD_3\underline{NH_2}$	6·0	9·8	6·8	4·4	9·9	7·7	1·6
CH_3NH_2 (overall)	7·2	10·6	7·0	4·2	10·8	8·7	3·0

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$

The atom abstracted is underlined.

The kinetic isotope effect of 1·9 kcal/mole exceeds considerably the zero-point energy difference of 1·2 kcal/mole for a single C-H and C-D stretching vibration. This is in accord with the results reported in the previous chapter for abstraction from CH_3OH and CD_3OH by both $CF_3\cdot$ and $CH_3\cdot$, and once more may indicate tunnelling.

As predicted in Chapter 4, depression of the A-factor is observed from the reaction:

$$CH_3NH_2 + CF_3\cdot \longrightarrow CH_3NH\cdot + CF_3H$$

due to dipolar repulsion between the molecule and the attacking radical. The effect is less pronounced than in the case of methanol, as would be expected from the Pauling electronegativities of oxygen and nitrogen (3·5 and 3·0 respectively). As will be seen from Table 34, Gray and Thynne report a low A-Factor for the corresponding methyl radical reaction. The overall activation energy

for hydrogen abstraction from CH_3NH_2 by methyl radicals exceeds that for $CF_3\cdot$ by 3·0 kcal/mole, in excellent agreement with the value established by Pritchard. For abstraction from the methyl group, however, the difference is 4·5 kcal/mole, while for the amino group it is only 1·6 kcal/mole, this low value being coupled with the low A-factor mentioned above. Severe analytical difficulties were encountered in the methyl radical work due to abstraction from the radical source, azomethane. (109)

$$CH_3\cdot + CH_3N_2CH_3 \longrightarrow CH_4 + CH_3N_2CH_2\cdot$$

For an equimolar mixture of azomethane and CD_3NH_2, the methane produced on photolysis at 164°C would be made up as follows:-

CH_4 from AZOMETHANE - 60%

CH_4 from CD_3NH_2 - 36%

CH_3D from CD_3NH_2 - 4%

Thus, as well as the error involved in analysing for such a small percentage of CH_3D, calculation of methane formed by abstraction from the amino group would involve relatively small differences between large quantities, with consequent accumulation of error. In particular a small error in the Arrhenius parameters for the above abstraction from the radical source would produce a considerably larger error in the parameters for the reaction

$$CH_3\cdot + CD_3NH_2 \longrightarrow CH_4 + CD_3NH\cdot$$

It seems likely, therefore, that the low A-factor reported for this reaction may be incorrect, particularly in view of the normal A-factor reported for abstraction of hydrogen from the hydroxyl group in methanol by $CH_3\cdot$. (114)

TABLE 35

Photolysis of TFMI in the Presence of Dimethylamine

RUN	T(°K)	t(sec)	Me_2NH	CF_3I	CF_3H	C_2F_6	R	$\frac{1000}{T}$	Log R
273	370·3	90	·295	·767	228	14·5	211	2·70	2·324
276	370·3	45	·554	·794	357	8·53	224	2·70	2·350
327	357·1	90	·694	·690	44·1	0·14	170	2·80	2·231
328	344·8	300	·183	1·83	25·8	0·84	156	2·90	2·194
330	344·8	900	·187	1·87	28·6	1·28	145	2·90	2·162
253	333·3	150	1·25	1·26	193	2·12	107	3·00	2·031
272	333·3	45	·481	1·25	328	40·6	108	3·00	2·035
275	333·3	45	·902	1·29	490	27·1	106	3·00	2·023
331	322·6	1100	·124	1·24	11·5	1·02	96·5	3·10	1·984
332	322·6	90	·479	1·36	30·3	0·52	88·6	3·10	1·947
333	322·6	900	·476	1·35	31·7	0·45	102	3·10	2·009
271	312·7	90	·591	1·54	307	54·2	72·2	3·20	1·858
336	303·0	300	·345	1·66	18·8	0·75	63·5	3·30	1·803
337	303·0	1500	·359	1·73	13·8	0·39	63·5	3·30	1·802

Me_2NH and CF_3I are in 10^{-6} mole cm^{-3}

CF_3H and C_2F_6 are in 10^{-12} mole $cm^{-3}sec^{-1}$.

The abstraction of hydrogen by $CF_3\cdot$ was also studied for dimethylamine, dimethylamine-d, and trimethylamine. The results are recorded in Tables 35 to 37 and presented graphically in Figs. 24, 26, 27 and 28. The Arrhenius parameters derived are listed in Table 38, along with those for the corresponding methyl radical reactions.

TABLE 36

Photolysis of TFMI in the Presence of Dimethylamine-d

RUN	T(°K)	t(sec)	Me_2ND	CF_3I	CF_3H	CF_3D	C_2F_6	R_H	R_D	$\frac{1000}{T}$	Log R_H	Log R_D
293	370·3	90	·496	1·00	226	40·8	8·64	155	28·0	2·70	2·190	1·447
269	370·3	300	·330	1·01	613	11·2	2·08	129	23·6	2·70	2·111	1·373
270	370·3	300	·234	·817	57	9·1	1·96	174	27·7	2·70	2·241	1·443
294	370·3	45	·463	1·12	197	37·5	7·54	155	29·5	2·70	2·190	1·470
298	357·1	90	·511	·765	95	20·7	5·21	81·1	17·8	2·80	1·909	1·250
301	344·8	90	·908	·641	94	18·0	1·59	82·0	15·7	2·90	1·914	1·196
295	333·3	90	·338	·814	75	13·2	7·01	83·1	14·7	3·00	1·920	1·167
297	333·3	90	·791	1·18	85	18·4	3·66	56·2	12·2	3·00	1·750	1·086
300	322·6	90	1·44	1·01	125	23·3	2·54	54·8	10·2	3·10	1·739	1·009

Me_2ND and CF_3I are in 10^{-6} mole cm^{-3}; CF_3H, CF_3D and C_2F_6 in 10^{-12} mole $cm^{-3}sec^{-1}$.

R_H refers to abstraction from the methyl groups, R_D to abstraction from ND.

TABLE 37

Photolysis of TFMI in the Presence of Trimethylamine

RUN	T(°K)	t(sec)	Me_3N	CF_3I	CF_3H	C_2F_6	R	$\frac{1000}{T}$	Log R
204	303·0	100	·175	1·76	67·1	18·8	88·5	3·30	1·947
207	303·5	45	1·01	1·00	390	21·6	83·3	3·30	1·921
205	322·5	100	·164	1·65	93·9	14·6	150	3·10	2·176
206	344·8	100	·174	1·76	150	14·0	230	2·90	2·362
210	370·3	45	1·12	1·11	1008	10·6	277	2·70	2·443
201	400·0	120	·221	1·19	351	12·5	449	2·50	2·652
211	400·0	45	·305	1·25	721	17·3	568	2·50	2·754
213	434·8	30	·387	1·59	1215	12·7	879	2·30	2·944
212	434·8	60	·266	1·09	684	9·95	815	2·30	2·911

Me_3N and CF_3I are in 10^{-6} mole cm^{-3};
CF_3H and C_2F_6 in 10^{-12} mole cm^{-3} sec^{-1}.

The activation energy requirements for the methyl radical abstractions shown in Table 38 exceed these of $CF_3\cdot$ by a little over 3 kcal/mole in every case, with little change in A.

TABLE 38

	TRIFLUOROMETHYL RADICALS			METHYL RADICALS			
	E	Log A	Log k_{164}	E	Log A	Log k_{164}	Ref.
$(CH_3)_2NH$	5·1	11·8	9·2	8·7	11·5	7·1	83
$(CH_3)_2N\underline{H}$	3·3	10·5	8·9	6·4	10·8	7·6	"
$(CH_3)_2N\underline{D}$	4·7	10·9	8·5	7·8	10·7	6·8	"
$(CH_3)_3N$	4·5	11·8	9·5	8·0	12·6	8·6	120, 121

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$

The hydrogen abstracted is underlined.

FIG. 27. HYDROGEN ABSTRACTION BY CF_3· RADICALS

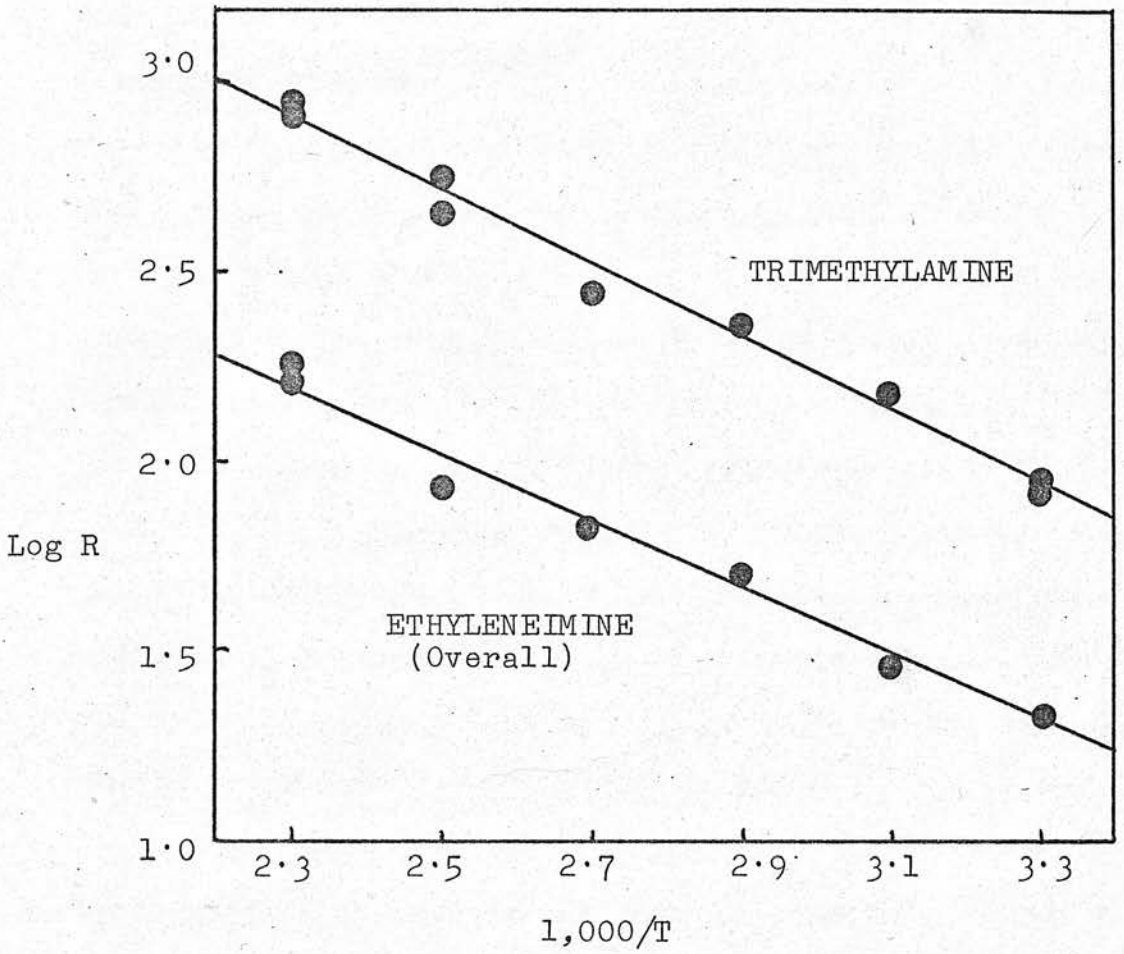
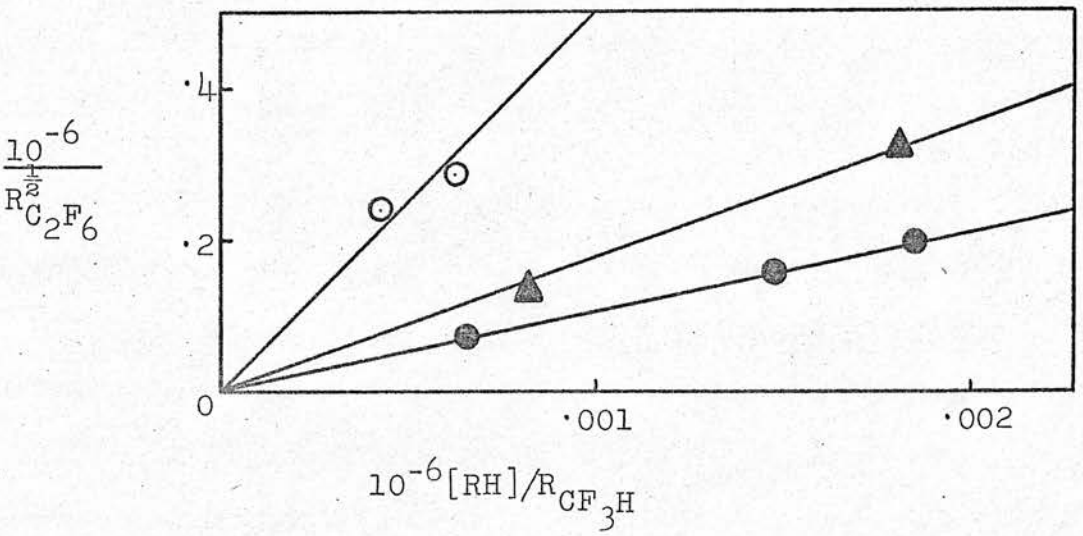


FIG. 28. TEST OF MECHANISM



○ Trimethylamine at 127°C; ▲ Ethyleneimine at 162°C;

◉ Dimethylamine (Overall Abstraction) at 60°C.

For either radical the activation energy for abstraction from the amine site in dimethylamine is around 2 kcal/mole lower than that for abstraction from the methyl groups. On a per-hydrogen atom basis the A-factor for methyl radical abstraction is the same for both sites, while for $CF_3\cdot$ there is again a suggestion of depression of the A-factor for abstraction from the polar position, although in this case the difference does not exceed the experimental error. Since the polarity of Me_2NH is considerably less than that of CH_3NH_2 or CH_3OH, less pronounced dipole interactions are to be expected. With both radicals, the activation energy for abstraction from the N-D group exceeds that for N-H by 1·4 kcal/mole, in good agreement with the zero-point energy difference of 1·3 kcal/mole.

Gray and Jones (122) have studied the abstraction of hydrogen from ethyleneimine by methyl radicals, and found that attack occurs almost exclusively at the NH position.

TABLE 39

Photolysis of TFMI in the Presence of Ethyleneimine

RUN	T(°K)	t(sec)	IMINE	CF_3I	CF_3H	C_2F_6	R	$\frac{1000}{T}$	Log R
284	303·1	45	·429	1·76	57·3	40·6	20·9	3·30	1·320
286	322·5	45	1·95	·771	110	3·96	28·5	3·10	1·455
285	344·8	45	·252	1·00	59·7	21·1	51·5	2·90	1·712
281	370·3	45	·384	1·58	136	26·9	68·0	2·70	1·833
287	400·0	90	1·54	·607	206	2·42	86·3	2·50	1·936
283	434·8	45	·387	1·59	470	55·2	163	2·30	2·212
290	434·8	90	·540	1·03	297	9·19	181	2·30	2·258

In the present work the overall kinetics of hydrogen abstraction by trifluoromethyl radicals have been studied (Table 39 and Figs. 27 and 28) and the results are presented in Table 40 along with those for methyl radicals.

TABLE 40

	E	Log A	Log k_{164}
$CH_3\cdot + \begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!NH \longrightarrow CH_4 + \begin{matrix}\cdot CH\\|\\CH_2\end{matrix}\!\!>\!NH$	10·1	11·4	6·3
$\longrightarrow CH_4 + \begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!N\cdot$	4·6	10·2	7·9
$\longrightarrow CH_4 + [C_2H_4N]\cdot$	4·8	10·3	7·9
$CF_3\cdot + \begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!NH \longrightarrow CF_3H + [C_2H_4N]\cdot$	4·1	11·0	8·9

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$

The Arrhenius parameters recorded in Table 40 strongly suggest that in the case of $CF_3\cdot$ there is appreciable attack at both sites. Both the activation energy and A-factor are higher than would be expected on the basis of the parameters reported by Gray and Jones for attack at the NH group alone, but lower than would be expected for abstraction from CH_2. A similar effect is observed for dimethylamine, where the ratio k_{METHYL}/k_{AMINO} at 164°C is six times greater for $CF_3\cdot$ attack than it is for methyl radicals. For methylamine the relative rate of attack at the methyl position is about twelve times greater for the polar radical. Once more this may be interpreted in terms of dipole-dipole repulsion, inhibiting attack at the polar site.

CHAPTER 7

As mentioned in Chapter 1, conflicting data have been reported for the photolysis of fluoroaldehydes, interpreted in terms of the following reaction scheme:-

$$R_fCHO + h\nu \longrightarrow R_f\cdot + CHO\cdot$$

$$R_f\cdot + R_fCHO \longrightarrow R_fH + R_fCO\cdot \quad (k_a)$$

$$R_f + R_f \longrightarrow R_{f_2} \ (k_c) \qquad R_f\cdot + CO$$

Arrhenius parameters reported for the hydrogen abstraction reaction are listed below.

TABLE 41.

ALDEHYDE	E	Log A	Log k_{164}	Ref.
CF_3CHO	8·4	11·7	7·5	Dodd and Smith
C_2F_5CHO	4·5	10·2	7·9	Pritchard et al.
n-C_3F_7CHO	4·0	9·9	7·9	" "

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$.

On the basis of their work with perfluoropropionaldehyde and perfluorobutyraldehyde, Pritchard, Miller and Foote (15) concluded that the activation energy reported by Dodd and Smith (17) for hydrogen atom abstraction from trifluoroacetaldehyde by $CF_3\cdot$ was "improbably high". In the present work the abstraction of hydrogen from these three fluoroaldehydes has been studied with methyl radicals from the thermal decomposition of DTBP and trifluoromethyl radicals generated by photolysis of HFA. (Tables 42 to 47 and Figs. 29 to 40).

TABLE 42. Photolysis of HFA/C_2F_5CHO Mixtures.

RUN	T(°K)	t(sec)	ALD	HFA	CF_3H	C_2F_6	C_2F_5H	C_3F_8	C_4F_{10}	Φ	R	$\frac{1000}{T}$	Log R
380	555·6	900	·250	·349	63·1	3·62	101	39·0	35·2	1·82	69·7	1·80	1·843
398	526·3	200	·522	·519	106	18·1	193	66·2	65·5	1·92	47·6	1·90	1·678
389	500·0	600	·300	·352	37·8	14·3	53·9	39·4	26·8	2·02	33·3	2·00	1·523
388	500·0	200	·500	·536	72·2	22·8	109	63·3	51·5	1·85	30·3	2·00	1·481
382	500·0	100	·111	·680	36·6	91·2	16·9	57·0	8·6	2·04	34·6	2·00	1·539
396	476·2	450	·287	·644	35·4	30·7	40·2	48·2	20·7	1·91	22·3	2·10	1·348
397	454·5	450	·688	·696	53·7	26·8	93·4	70·4	46·2	2·01	15·1	2·20	1·178
394	434·8	450	·399	·876	23·6	30·9	35·9	50·2	22·7	1·90	10·6	2·30	1·027
387	400·0	600	·676	·730	11·5	9·82	59·5	31·8	31·6	1·81	5·44	2·50	0·735
379	400·0	200	·157	2·36	9·98	79·4	11·6	46·7	7·2	1·95	7·13	2·50	0·853
385	400·0	600	·085	·587	3·78	52·1	5·3	28·0	4·2	1·90	6·17	2·50	0·791
384	400·0	200	·160	·989	8·53	90·4	11·6	51·5	7·1	2·04	5·61	2·50	0·749
380	400·0	600	·093	1·61	6·11	72·4	8·2	38·5	4·9	2·04	7·72	2·50	0·887
378	400·0	200	·459	1·40	17·6	26·7	37·8	48·4	20·8	2·06	7·45	2·50	0·872
374	400·0	450	·555	1·74	17·3	28·1	32·6	49·9	23·8	1·92	5·54	2·50	0·743
400	384·6	450	·724	·701	8·68	8·63	51·2	34·6	34·4	2·01	4·08	2·60	0·610
393	370·4	450	·553	1·18	8·21	22·8	31·9	49·3	26·1	2·03	3·11	2·70	0·493
399	357·1	450	1·19	1·13	5·41	4·47	60·0	25·8	41·1	1·91	2·15	2·80	0·332

ALD. and HFA are in 10^{-6} mole cm^{-3};

CF_3H, C_2F_6, C_2F_5H, C_3F_8 and C_4F_{10} are in 10^{-12} mole $cm^{-3}sec^{-1}$.

TABLE 43.

Photolysis of HFA/C_3F_7CHO Mixtures

RUN	T(°K)	t(sec)	ALD.	HFA	CF_3H	C_2F_6	R	$\frac{1000}{T}$	Log R
417	555·6	200	·500	·991	162	30·4	60·8	1·80	1·784
416	555·6	200	·326	1·20	136	37·3	71·5	1·80	1·854
421	526·3	200	·463	·918	126	25·5	55·2	1·90	1·741
412	526·3	200	·170	2·11	97·0	148	49·9	1·90	1·697
411	476·2	200	·269	3·33	92·1	245	22·7	2·10	1·355
415	434·8	300	·593	2·19	70·1	103	11·9	2·30	1·074
419	400·0	900	·915	1·81	36·2	41·6	6·25	2·50	0·796
418	400·0	100	·737	1·46	31·9	43·1	6·61	2·50	0·820
414	400·0	450	·391	1·44	19·7	73·4	5·96	2·50	0·775
409	400·0	900	·890	·859	23·4	12·2	7·61	2·50	0·881
408	400·0	150	1·44	1·39	37·6	11·7	7·66	2·50	0·884

ALD. and HFA are in 10^{-6} mole cm^{-3}

CF_3H and C_2F_6 are in 10^{-12} mole $cm^{-3}sec^{-1}$.

TABLE 44.

Photolysis of HFA/CF_3CHO Mixtures

RUN	T(°K)	t(sec)	ALD.	HFA	CF_3H	C_2F_6	R	$\frac{1000}{T}$	Log R
444	555·6	200	2·47	0·00	1624	124	63·2	1·80	1·800
445	555·6	25	1·34	0·00	940	94·3	73·2	1·80	1·864
437	555·6	100	·339	1·67	332	255	64·4	1·80	1·808
438	555·6	25	·235	1·16	258	217	75·4	1·80	1·877
439	555·6	100	·162	1·64	187	267	75·1	1·80	1·875
432	526·3	200	·119	1·27	66·4	193	42·3	1·90	1·626
436	526·3	100	·516	2·54	351	290	41·3	1·90	1·616
431	500·0	200	·183	1·96	72·5	266	25·3	2·00	1·402
430	476·2	200	·174	1·86	47·6	254	17·6	2·10	1·245
435	476·2	200	·321	1·58	85·8	225	18·3	2·10	1·262
429	454·5	200	·168	1·79	29·3	242	11·4	2·20	1·057
428	434·8	200	·162	1·73	21·0	250	8·3	2·30	0·921
434	434·8	300	·308	1·52	32·7	220	7·3	2·30	0·861
427	416·7	200	·144	1·53	14·0	228	6·5	2·40	0·813
442	416·7	200	·310	3·15	45·0	346	7·9	2·40	0·898
422	400·0	450	5·14	0·00	206	60·0	5·2	2·50	0·718
424	400·0	300	·246	1·54	14·4	112	5·6	2·50	0·745
425	400·0	100	·413	2·59	30·3	213	5·1	2·50	0·704
433	400·0	200	·328	1·61	21·5	222	4·4	2·50	0·646
441	400·0	450	·250	2·54	24·9	289	6·0	2·50	0·777

ALD. and HFA are in 10^{-6}mole cm^{-3},
CF_3H and C_2F_6 in 10^{-12}mole $cm^{-3}sec^{-1}$.

The runs performed at 400 and 417°C were not included in the least-squares calculation of Arrhenius Parameters.

TABLE 45

Thermal Decomposition of DTBP in the Presence of Trifluoroacetaldehyde

T(^{o}K)	t(sec)	ALD	DTBP	CH_4	C_2H_6	R	$\frac{1000}{T}$	Log R
401·1	2500	0·59	0·28	2·23	0·75	4·21	2·49	0·62
401·5	480	0·49	0·24	2·45	1·27	4·33	2·49	0·64
405·2	750	0·53	0·40	5·02	2·81	5·43	2·47	0·73
409·7	600	0·69	0·35	7·86	4·34	5·29	2·44	0·72
415·1	1200	0·59	0·27	9·50	4·74	7·19	2·41	0·86
421·4	240	0·59	0·24	21·6	20·1	7·95	2·37	0·90
421·4	300	0·64	0·36	21·6	14·7	8·48	2·37	0·93
421·4	200	0·57	0·36	21·2	18·4	8·30	2·37	0·92
429·2	180	0·56	0·28	35·5	40·5	9·64	2·33	0·98
429·2	200	0·58	0·27	41·0	49·6	9·74	2·33	0·99
435·6	200	0·43	0·16	32·1	53·1	10·1	2·30	1·00
436·2	120	0·68	0·30	94·3	176	10·1	2·29	1·00
440·9	100	0·61	0·29	111	194	12·6	2·27	1·10
443·8	120	0·65	0·30	143	278	12·7	2·25	1·10
444·2	120	0·53	0·24	95·0	134	15·1	2·25	1·18
444·8	150	0·53	0·22	101	254	11·5	2·25	1·06

Units as in Table 47.

TABLE 46.

Thermal-Decomposition of DTBP in the Presence of Perfluoropropionaldehyde

T(°K)	t(sec)	ALD	DTBP	CH_4	C_2H_6	R	1000/T	Log R
398·2	3600	0·22	0·12	0·91	0·27	7·94	2·51	0·90
398·2	1800	0·23	0·15	1·42	0·51	7·61	2·51	0·88
403·0	600	0·26	0·17	2·48	1·35	7·87	2·48	0·90
403·2	540	0·26	0·17	2·61	1·33	8·35	2·48	0·92
408·2	1200	0·19	0·13	2·33	1·41	10·2	2·45	1·01
408·2	900	0·25	0·19	4·49	2·20	12·6	2·45	1·10
413·0	480	0·23	0·11	4·74	2·47	13·0	2·42	1·11
413·2	480	0·30	0·16	6·33	2·69	12·4	2·42	1·09
418·4	420	0·30	0·19	11·4	7·11	14·0	2·39	1·15
423·2	480	0·26	0·16	14·2	12·8	15·1	2·36	1·18
428·2	420	0·22	0·15	15·6	14·1	18·0	2·34	1·26
433·6	480	0·19	0·10	16·6	19·1	20·0	2·31	1·30
438·2	240	0·18	·084	18·5	19·3	23·0	2·28	1·36
438·2	300	0·17	0·10	22·0	26·5	23·7	2·28	1·37

Units as in Table 47.

TABLE 46.

Thermal-Decomposition of DTBP in the Presence of Perfluoropropionaldehyde

T(°K)	t(sec)	ALD	DTBP	CH_4	C_2H_6	R	1000/T	Log R
398·2	3600	0·22	0·12	0·91	0·27	7·94	2·51	0·90
398·2	1800	0·23	0·15	1·42	0·51	7·61	2·51	0·88
403·0	600	0·26	0·17	2·48	1·35	7·87	2·48	0·90
403·2	540	0·26	0·17	2·61	1·33	8·35	2·48	0·92
408·2	1200	0·19	0·13	2·33	1·41	10·2	2·45	1·01
408·2	900	0·25	0·19	4·49	2·20	12·6	2·45	1·10
413·0	480	0·23	0·11	4·74	2·47	13·0	2·42	1·11
413·2	480	0·30	0·16	6·33	2·69	12·4	2·42	1·09
418·4	420	0·30	0·19	11·4	7·11	14·0	2·39	1·15
423·2	480	0·26	0·16	14·2	12·8	15·1	2·36	1·18
428·2	420	0·22	0·15	15·6	14·1	18·0	2·34	1·26
433·6	480	0·19	0·10	16·6	19·1	20·0	2·31	1·30
438·2	240	0·18	·084	18·5	19·3	23·0	2·28	1·36
438·2	300	0·17	0·10	22·0	26·5	23·7	2·28	1·37

Units as in Table 47.

TABLE 47

Thermal Decomposition of DTBP in the Presence of Perfluorobutyraldehyde

T(°K)	t(sec)	ALD	DTBP	CH_4	C_2H_6	R	1000/T	Log R
398·2	3600	0·31	0·14	1·15	0·28	6·85	2·51	0·84
398·4	1800	0·33	0·14	1·26	0·34	6·46	2·51	0·81
403·2	1620	0·26	0·17	1·51	0·54	7·60	2·48	0·88
403·2	1200	0·28	0·17	2·28	0·87	8·54	2·48	0·93
408·4	1200	0·25	0·12	2·48	0·74	11·6	2·45	1·06
408·2	1800	0·32	0·15	3·33	0·97	10·3	2·45	1·01
413·2	900	0·24	0·14	4·80	2·25	11·2	2·42	1·05
418·4	660	0·24	0·14	6·88	4·28	13·3	2·39	1·12
423·2	480	0·25	0·13	10·4	6·56	16·1	2·36	1·21
428·6	360	0·22	0·15	16·7	17·8	17·8	2·33	1·25
433·2	360	0·18	0·10	16·5	19·1	20·2	2·31	1·31
438·4	300	0·19	0·09	24·2	28·7	23·2	2·28	1·37

ALD. and DTBP are in 10^{-6} mole cm^{-3}, CH_4 and C_2H_6 in 10^{-12} mole $cm^{-3}sec^{-1}$.

CH_4, the rate of formation of methane, has been corrected for the contribution arising by abstraction from the radical source, and refers only to abstraction from CHO.

PHOTOLYSIS OF DTBP IN THE PRESENCE OF FLUOROALDEHYDES

FIG. 29. $CH_3\cdot + CF_3CHO \longrightarrow CH_4 + CF_3CO\cdot$

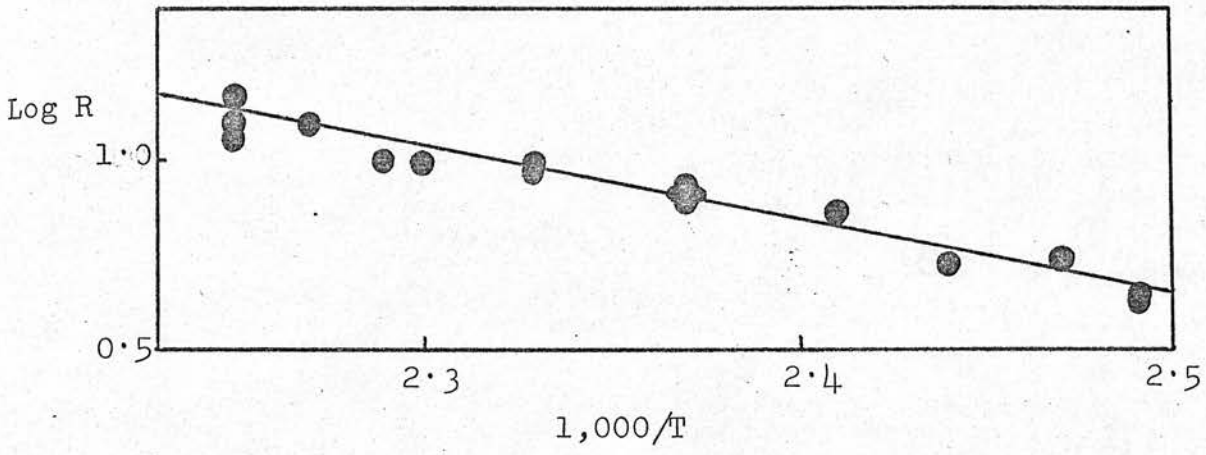


FIG. 30. $CH_3\cdot + C_2F_5CHO \longrightarrow CH_4 + C_2F_5CO\cdot$

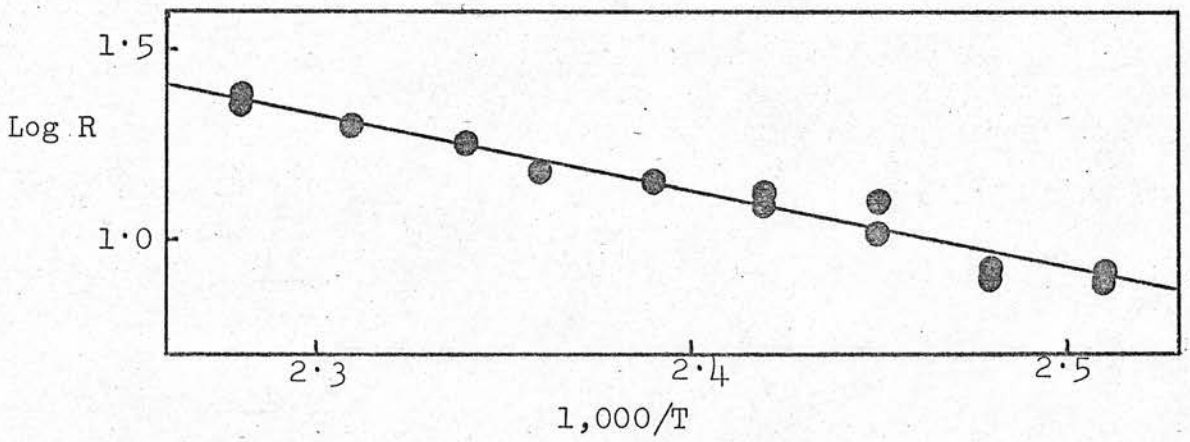
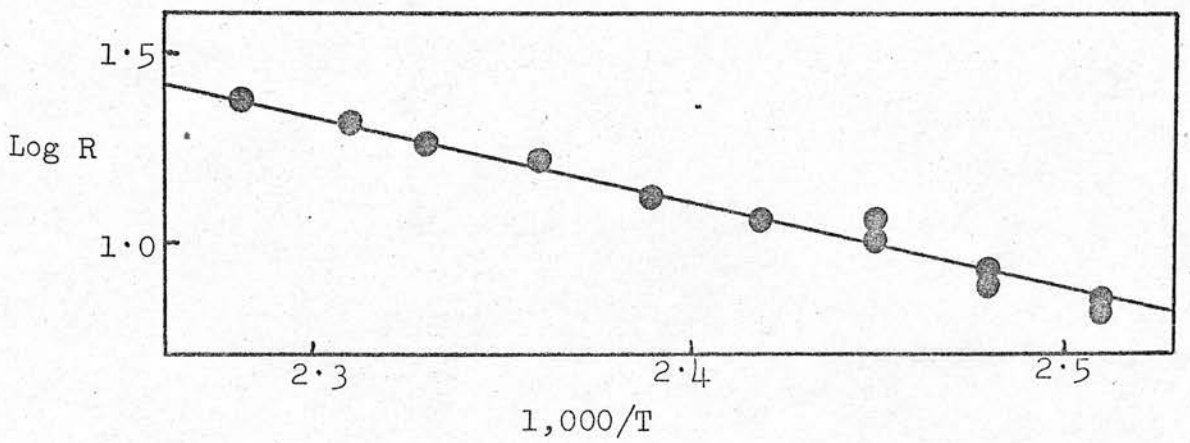


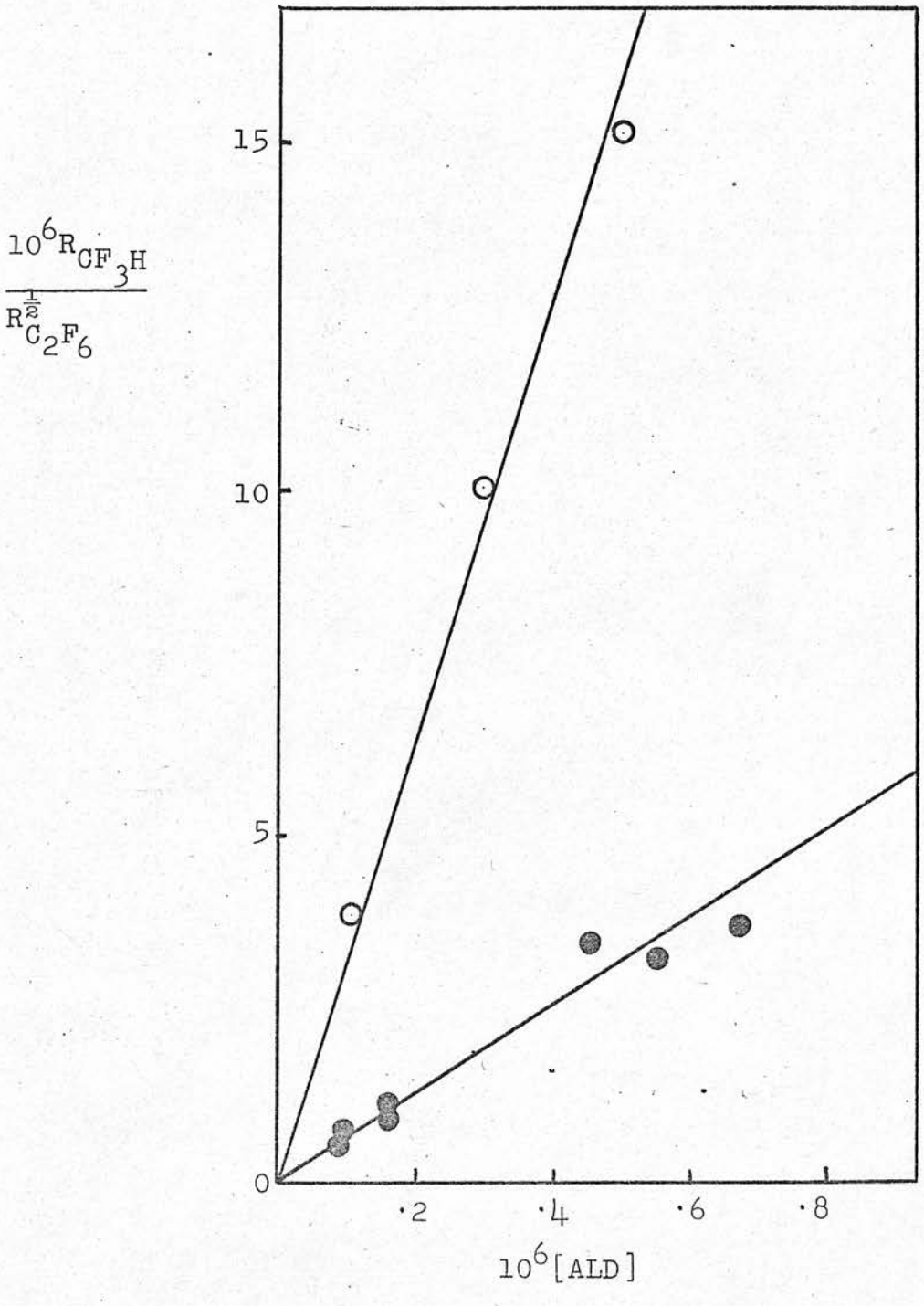
FIG. 31. $CH_3\cdot + n\text{-}C_3F_7CHO \longrightarrow CH_4 + n\text{-}C_3F_7CO\cdot$



PHOTOLYSIS OF HFA/C_2F_5CHO MIXTURES

- Test of Mechanism for CF_3H Formation -

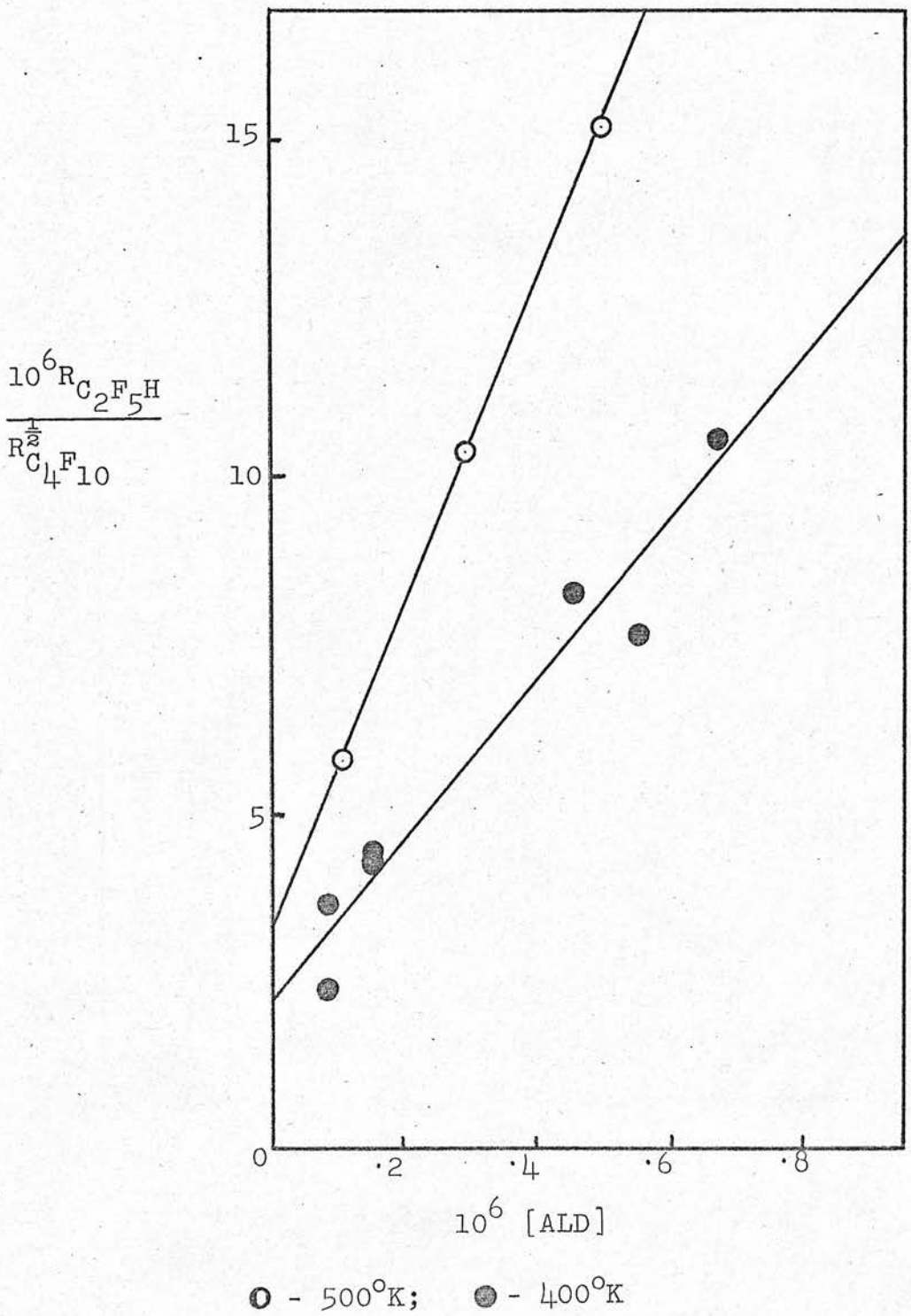
FIG. 32.



PHOTOLYSIS OF HFA/C_2F_5CHO MIXTURES.

- Test of Mechanism for C_2F_5H Formation -

FIG. 33.



PHOTOLYSIS OF C_2F_5CHO (AT 302 ± 3°K)

- From Results Published by Pritchard, Miller and Foote (Ref. 15) -

TEST OF MECHANISM FOR C_2F_5H FORMATION

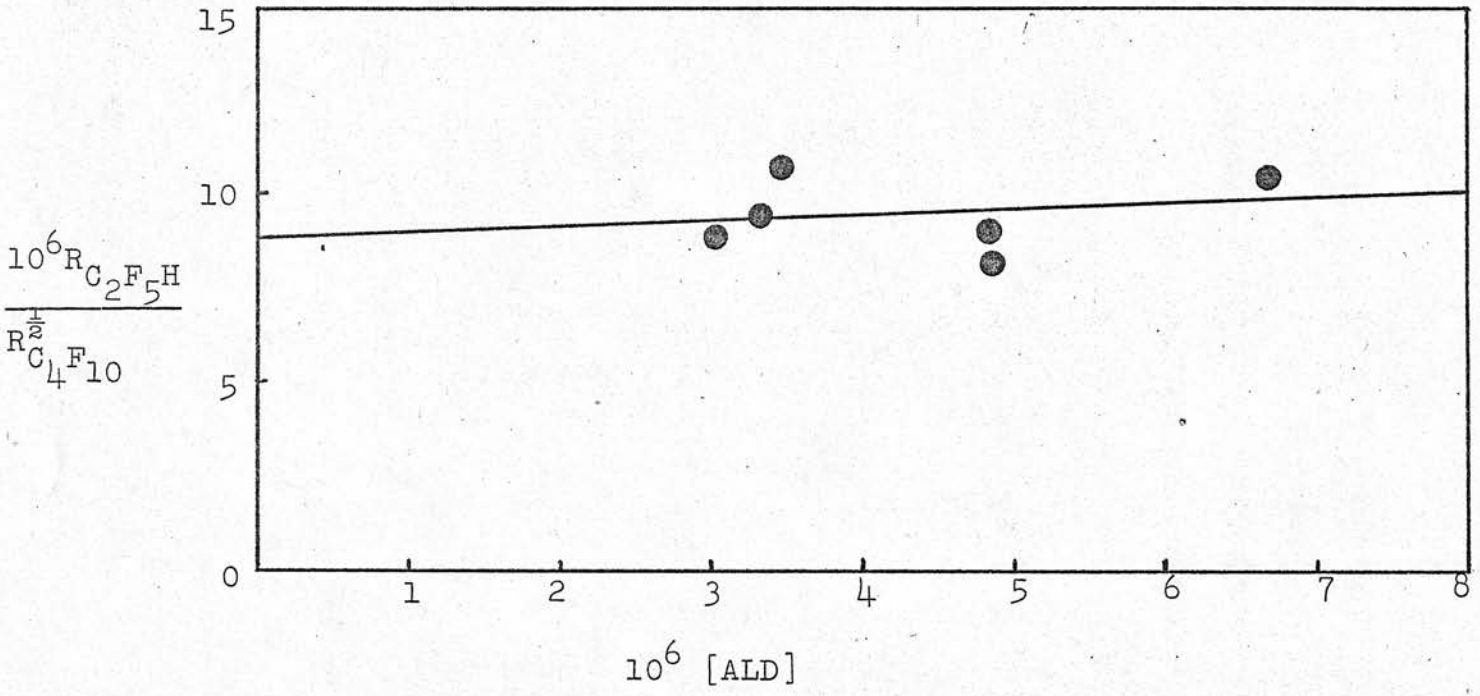


FIG 34.

From Figs. 32 and 33 it is evident that while fluoroform produced on photolysis of mixtures of HFA and C_2F_5 CHO may be accounted for by the reactions

$$CF_3\cdot + C_2F_5CHO \longrightarrow CF_3H + C_2F_5CO\cdot \quad (k_a)$$

and $$CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6 \quad (k_c)$$

pentafluoroethane formation cannot be explained solely in terms of the corresponding reactions of the perfluoroethyl radical. Analysis of published data (15) for the photolysis of C_2F_5CHO supports this conclusion (Fig. 34). It is suggested that C_2F_5H is formed intramolecularly as a primary photolytic process, so that the reactions leading to measured products are:-

$$R_fCHO + h\nu \rightarrow \underline{R_fH} + CO \quad I$$

$$R_fCHO + h\nu \rightarrow R_f\cdot + CHO\cdot \quad II$$

$$R_fCHO \xrightarrow{CF_3\cdot} \underline{CF_3H} + R_fCO\cdot$$

$$R_fCHO \xrightarrow{R_f\cdot} \underline{R_fH} + R_fCO\cdot$$

$$\underline{CF_3H} + R_fCO\cdot \rightarrow R_f\cdot + CO \quad \underline{R_fH} + R_fCO\cdot \rightarrow R_f\cdot + CO \quad \text{(Chain)}$$

$$CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6$$

$$CF_3\cdot + R_f\cdot \longrightarrow CF_3R_f \qquad R_f\cdot + R_f \longrightarrow R_{f_2}$$

The observed cross-combination ratio for $C_2F_5\cdot$ and $CF_3\cdot$ was $2\cdot0 \pm \cdot1$, (Independent of Temperature).

At low temperatures Pritchard and his colleagues observed a wide scatter of values of R ; this may be explained in terms of the greater relative importance of the intramolecular formation of C_2F_5H for low values of k_a, shown in Fig. 33.

By raising disproportionately the apparent value of k_a at low temperatures, the occurrence of reaction I will lead to low Arrhenius parameters for the abstraction reaction, as found by Pritchard.

As a further test of the above reaction scheme a few runs were performed in which C_2F_5CHO was photolysed in the presence of nitric oxide, perfluoroethyl radicals being removed from the system by the reaction

$$C_2F_5\cdot + NO \longrightarrow C_2F_5NO$$

While C_4F_{10} formation was inhibited completely, C_2F_5H was detected in appreciable amounts. In a typical inhibited run at 400°K the C_2F_5H yield was 25% of that for comparable runs without NO. Similar results were observed for CF_3CHO and C_3F_7CHO. Since in unscavenged runs decarbonylation of $R_fCO\cdot$ is likely to be the principal source of $R_f\cdot$, this relatively low degree of R_fH inhibition indicates that reaction I is at least comparable with II as a mode of photodecomposition of R_fCHO. In the case of trifluoroacetaldehyde it is not possible to distinguish between CF_3H arising from abstraction and that formed intramolecularly. Although high relative concentrations of HFA were used, distinct curvature of the Arrhenius plot was observed below 150°C, (Fig. 35), as found by Dodd and Smith for photolysis of the aldehyde alone, while even at 280°C there is evidence (Figs. 36 and 37) that the intramolecular reaction is contributing significantly to the total yield of fluoroform.

PHOTOLYSIS OF HFA/CF_3CHO MIXTURES: ARRHENIUS PLOT

All Fluoroform is attributed to the Reaction:

$$CF_3\cdot + CF_3CHO \longrightarrow CF_3H + CF_3CO\cdot$$

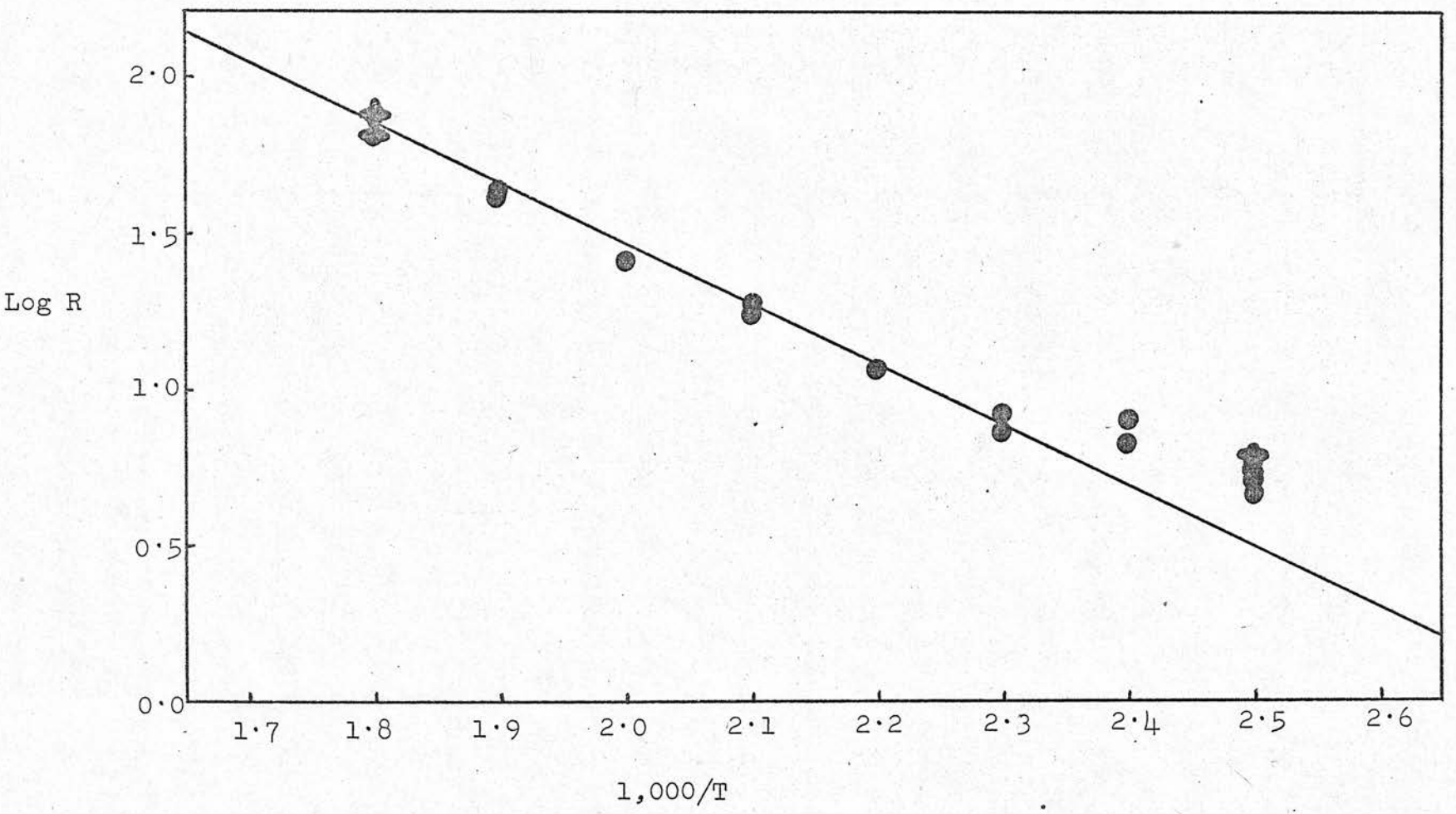
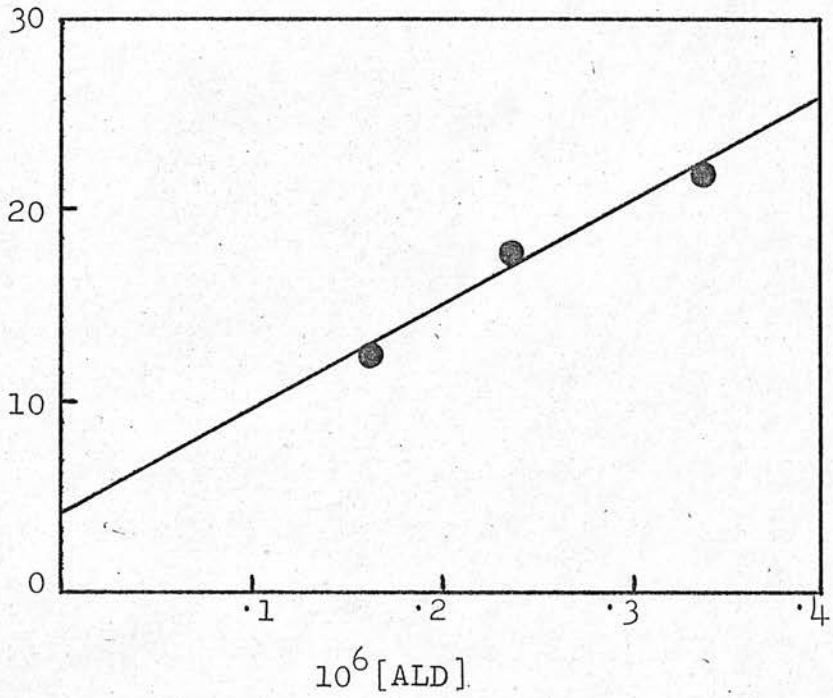


FIG. 35.

PHOTOLYSIS OF HFA/CF_3CHO MIXTURES (AT 556°K)

- Test of Mechanism of CF_3H Formation -

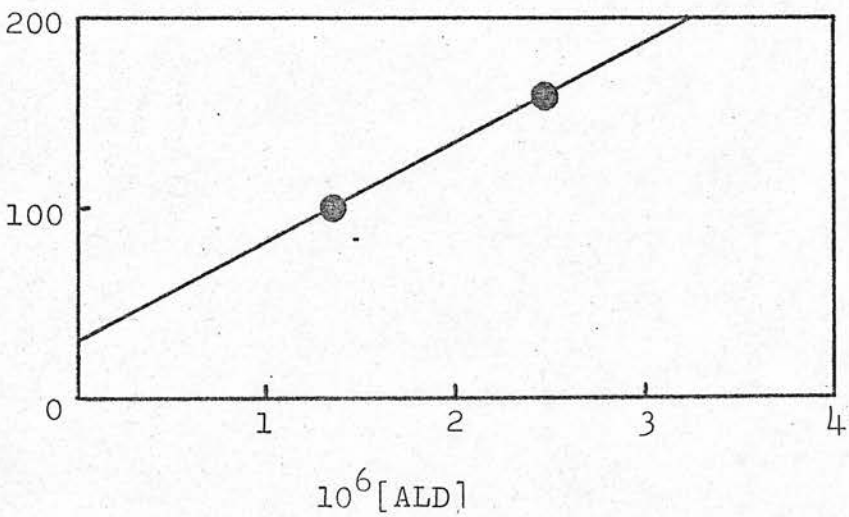
FIG. 36.



PHOTOLYSIS OF CF_3CHO (AT 556°K)

- Test of Mechanism of CF_3H Formation -

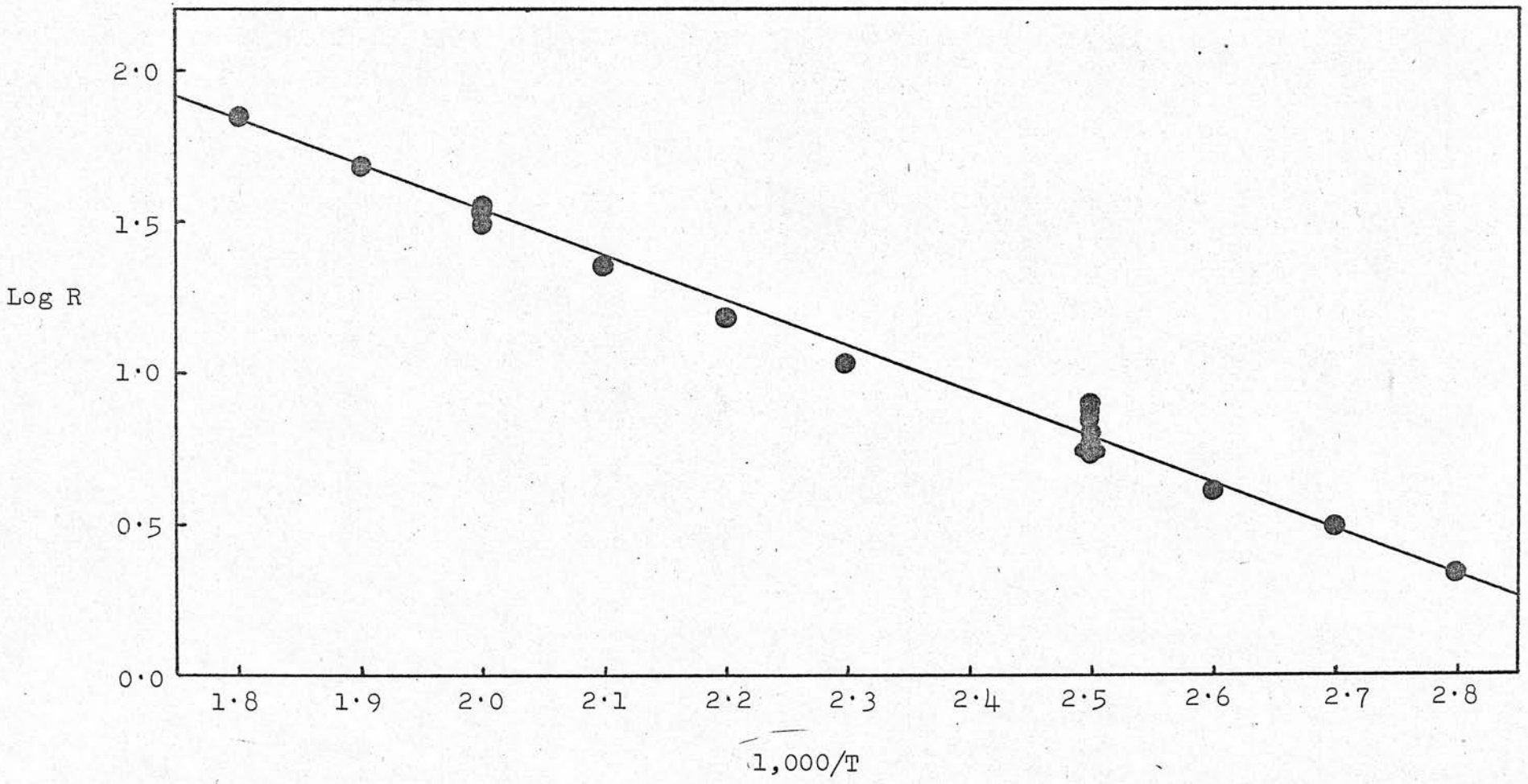
FIG. 37.



PHOTOLYSIS OF HFA/C_2F_5CHO MIXTURES: ARRHENIUS PLOT FOR:-

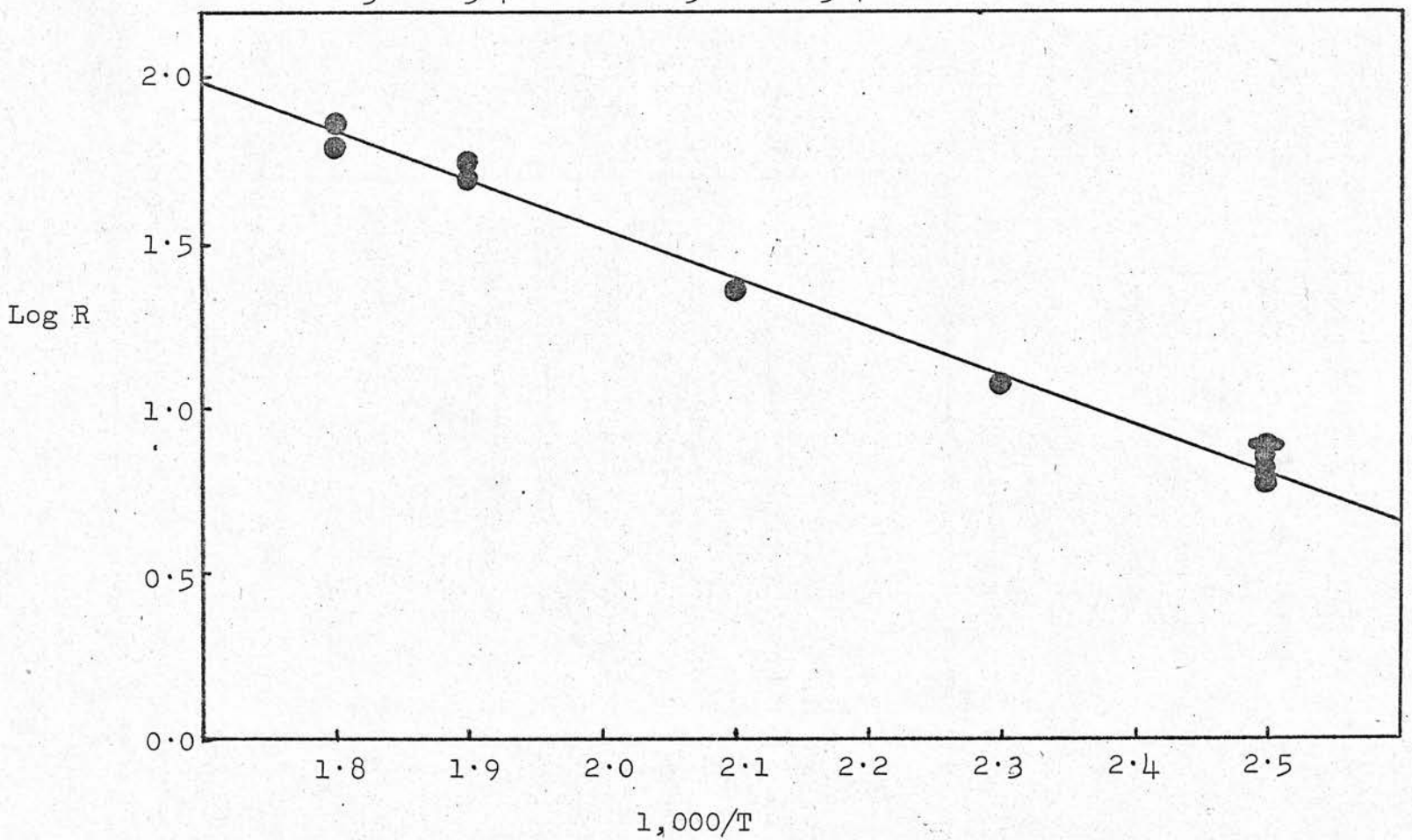
$CF_3\cdot + C_2F_5CHO \longrightarrow CF_3H + C_2F_5CO.$

FIG. 38.



PHOTOLYSIS OF HFA/C_3F_7CHO MIXTURES: ARRHENIUS PLOT FOR: FIG. 39.

$$CF_3\cdot + C_3F_7CHO \longrightarrow CF_3H + C_3F_7CO\cdot$$



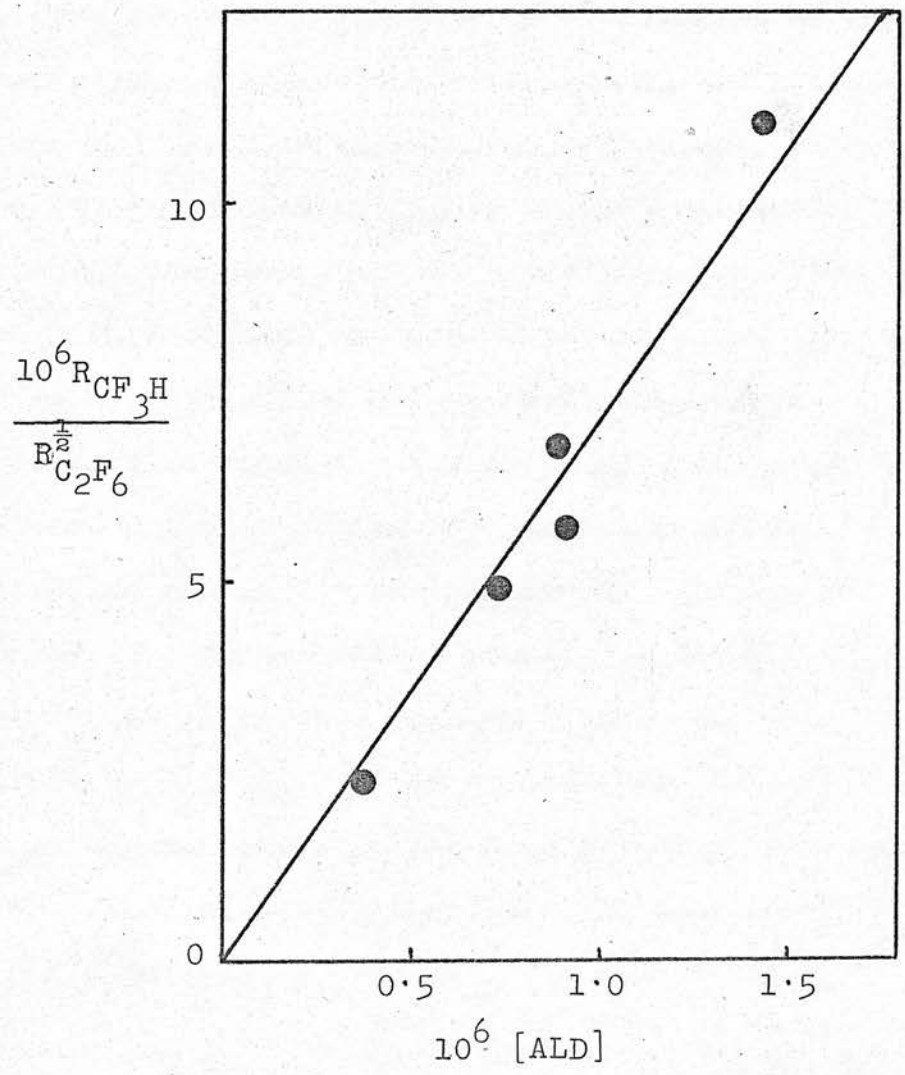
PHOTOLYSIS OF HFA/C_3F_7CHO MIXTURES.

TEST OF MECHANISM

$$C_3F_7CHO + CF_3\cdot \longrightarrow C_3F_7CO\cdot + CF_3H$$

$$CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6$$

FIG. 40.



Arrhenius parameters calculated for the substantially linear portion of the plot above 150°C are in excellent agreement with those reported by Dodd and Smith.

E	Log A	Log k_{164}	
8·4	11·7	7·5	Dodd and Smith.
8·8	12·0	7·6	This Work.

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$.

In view of the uncertainty which in this case exists over the relative importance of intramolecular elimination, these parameters should not be regarded as entirely reliable. No such uncertainty, of course, exists in the case of $CF_3\cdot$ attack on higher perfluoroaldehydes. The Arrhenius parameters obtained for these reactions are listed in Table 48, together with the parameters obtained for methyl radical attack on perfluoroaldehydes. For purposes of comparison, Arrhenius parameters are also included for abstraction from normal aldehydes. The activation energy for abstraction of an aldehydic hydrogen atom by $CF_3\cdot$ appears to be around 3·5 kcal/mole lower than that for $CH_3\cdot$, in good agreement with the value established by Pritchard (77). It is evident from Table 48 that the Arrhenius parameters for radical attack on RCHO increase as the complexity of R increases, in the order

$$H < Me < CF_3 < i\text{-}Pr < C_2F_5 < t\text{-}Bu < n\text{-}C_3F_7,$$

although log k_{164} remains essentially constant at 8·0 $\pm$ ·2 (k is in $mole^{-1}cm^3sec^{-1}$), except for formamide which reacts more slowly by a factor of ten.

TABLE 48

Hydrogen Atom Abstraction from Aldehydes

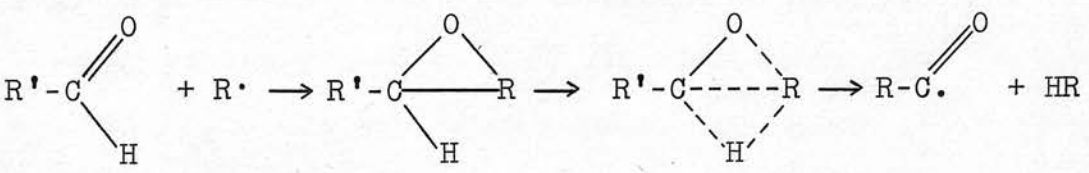
	Methyl Radicals				Trifluoromethyl Radicals			
	E	Log A	Log k_{164}	Ref.	E	Log A	Log k_{164}	Ref.
CF_3CHO	8·7	12·1	7·8	p				
C_2F_5CHO	9·8	12·9	8·0	p	6·7	11·1	7·7	p
n-C_3F_7CHO	10·3	13·2	8·0	p	6·6	11·1	7·8	p
HCHO	6·6	10·3	7·0	154,155				
CH_3CHO	7·6	11·9	8·1	155,125	4·2	10·8	8·7	17
i-C_3H_7CHO	8·7	12·6	8·2	125				
t-C_4H_9CHO	10·2	13·0	7·9	125				
n-C_4H_9CHO	8·0	12·1	8·1	125				

(p - This Work)

E is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$.

For normal aldehydes Trotman-Dickinson has suggested that the observed variation in Arrhenius parameters is spurious [153], and has attributed it to experimental error. However, since the same general trend is observed for fluoroaldehydes, formates and formamides (126, 127, 128, 129) this explanation seems rather unsatisfactory, especially since in many cases the variation involved is considerably outwith any reasonable estimate of likely experimental error. It should also be noted that the A-factors observed for the more complex aldehydes are far higher than have been reported for any other hydrogen abstractions. The following tentative explanation of these observations is suggested.

It is well established (59, 130, 131) that free radicals will readily associated with the electrons of a double bond to form a π-complex, this being the first stage in the addition of radicals to unsaturated molecules. Szwarc (59, 131) has suggested that this process occurs with zero activation energy. The stability of such complexes has been demonstrated by E.S.R. studies (130). It would therefore seem possible that the principal mode of radical attack involves the carbonyl group rather than the hydrogen atom, with subsequent intramolecular elimination of RH.



Reactants π-complex Activated complex Products

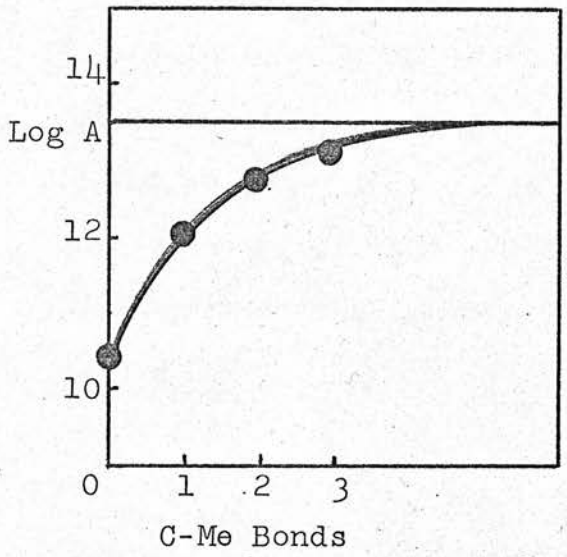
The probability of transition to the activated complex must evidently depend upon the life-time of the π-complex, which in turn must depend on the availability of oscillators capable of removing energy from the reactive centre. This may be correlated with the observed A-factors for the reaction: $CH_3\cdot + R'CHO \longrightarrow CH_4 + R'CO\cdot$

R':	H	Me	Et	n-Pr	n-Bu	Me_2CH	Me_3C
Log A:	10·3	11·9	12·0	11·8	12·1	12·6	13·0

Comparison of the values for n-propyl and i-propyl, and for n-butyl and t-butyl, suggests that the number of carbon-carbon oscillators adjacent to the aldehyde group is of importance, rather than the size of the alkyl group. This is further illustrated by the observed A-factors for CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9 where no systematic variation occurs, and is shown graphically in Fig. 41. As the number of available oscillators of suitable frequency for near-resonance transfer of energy from the reactive centre increases, log A appears to approach the value of around 13·4, found for radical combination. In view of the likelihood that π-complex formation and radical combination both have zero activation energy, it is not unreasonable to suggest that the two will take place at comparable rates. If this is the case, then Fig. 41 indicates that with increasing stability of the π-complex the probability of ultimate successful transition to the activated complex approaches unity for systems possessing the necessary energy indicated in Fig. 42.

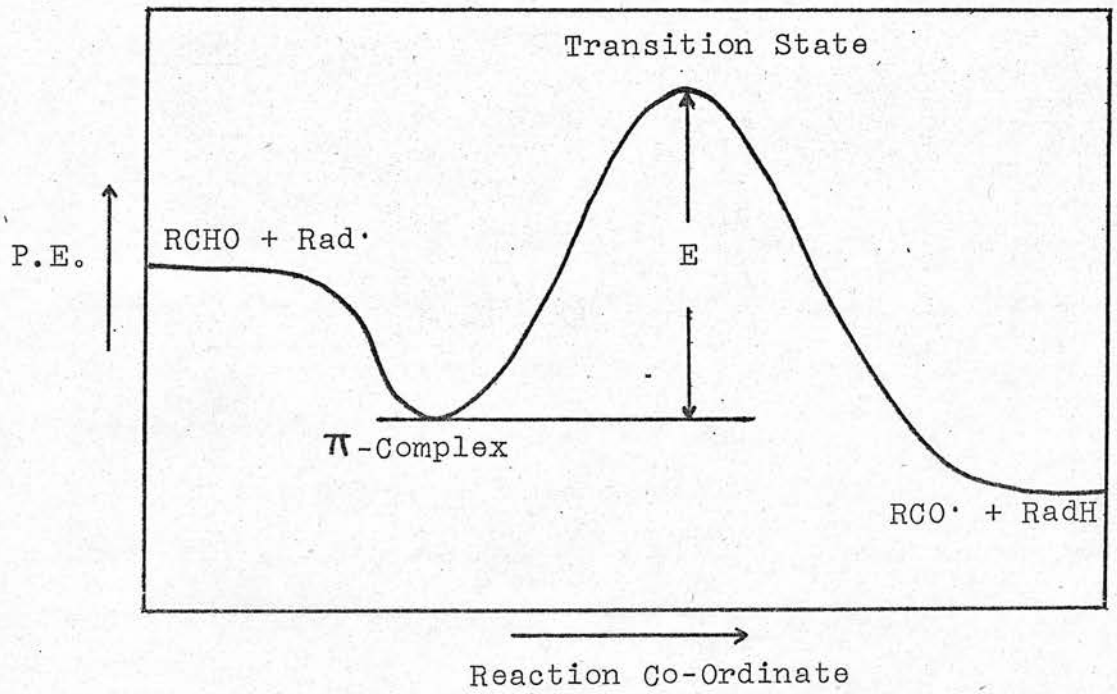
$$RCHO + CH_3\cdot \longrightarrow RCO\cdot + CH_4$$

FIG. 41.

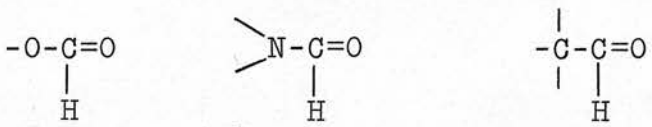


	C-Me Bonds	Log A
HCHO	0	10·3
MeCHO	1	11·9
Me_2CHCHO	2	12·6
Me_3CCHO	3	13·0

FIG. 42.



It is evident that the energy required will increase with increasing well-depth, i.e. with increasing stability of the π-complex, which is in accord with the observed trend in activation energies from HCHO to t-BuCHO. Extending this treatment to formates and formamides, it would be reasonable to expect a decrease in stability of the π-complex (and consequent decrease in A-Factor for abstraction) due to withdrawal of π-electrons, in the order:-



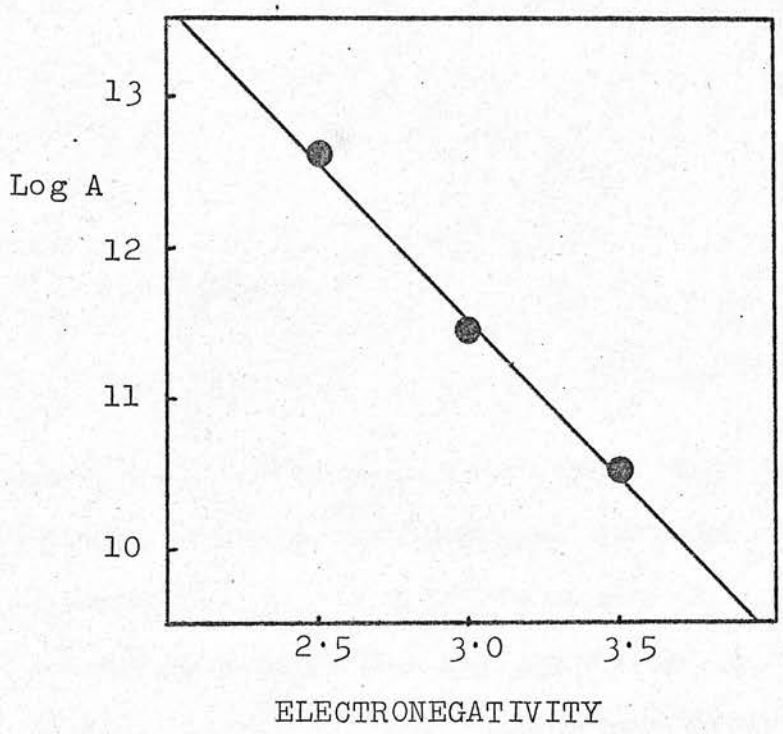
This is in fact found to be the case, as is shown in Fig. 43 where Log A is plotted against the Pauling electronegativity of the atom adjacent to the carbonyl group. Similar destabilisation of the π-complex by electron withdrawal is shown by the lower Arrhenius parameters for attack by the highly electronegative $CF_3\cdot$ radicals relative to those for $CH_3\cdot$.

While the proposed mechanism is, of course, highly speculative, it appears to provide a cohesive explanation of the observed variations in the Arrhenius parameters for hydrogen abstraction from RCHO brought about by changes in R, and also to account for the extremely high A-factors for abstraction from complex aldehydes.

In the course of this work an attempt was made to study the kinetics of hydrogen abstraction by $CF_3\cdot$ from non-fluorinated aldehydes. A few preliminary runs were

TRIFLUOROMETHYL RADICAL ATTACK ON CHO

FIG. 43.



In Fig. 43. Log A for the Reaction

$$RXCHO + CF_3\cdot \longrightarrow RXCO\cdot + CF_3H$$

is plotted against the Electronegativity of the Atom X, adjacent to the CHO group.

In order to keep the effects of energy transfer as constant as possible the compounds considered are:-

		Log A	E
ETHYL FORMATE	: C_2H_5OCHO	10·5	8·2
DIMETHYL FORMAMIDE	: C_2H_6NCHO	11·4	8·3
ISOBUTYRALDEHYDE	: C_2H_7CCHO	12·6	8·7

PAULING ELECTRONEGATIVITIES

C - 2·5; N - 3·0; O - 3·5.

performed in which HFA was photolysed in the presence or propionaldehyde, the results being interpreted in terms of the following reactions:-

$$CF_3\cdot + C_2H_5CHO \longrightarrow CF_3H + C_2H_5CO\cdot$$

$$C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_4H_{10}$$

$$C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_2H_4 + C_2H_6$$

$$C_2H_5CO\cdot \longrightarrow C_2H_5\cdot + CO$$

$$C_2H_5\cdot + C_2H_5CHO \longrightarrow C_2H_6 + C_2H_5CO\cdot$$

$$CF_3 + CF_3\cdot \longrightarrow C_2F_6 \qquad C_2H_5\cdot + CF_3\cdot \longrightarrow C_2H_5CF_3$$

It was immediately evident, however, that this scheme was not obeyed. While the disproportion/combination ratio for ethyl radicals is ·14, values of $R_{C_2H_4}/R_{C_4H_{10}}$ ranged from ·02 to ·45, while the cross-combination ratio for $C_2H_5\cdot$ and $CF_3\cdot$ varied with temperature between 3·3 and 4·5. Values calculated for R at constant temperature showed marked make-up dependence. To explain these observations the following additional reactions are proposed.

$$C_2H_5\cdot + CF_3\cdot \longrightarrow C_2H_4 + \underline{CF_3H}$$

$$C_2H_4 \xrightarrow{CF_3\cdot} C_2H_4CF_3\cdot$$

$$C_2H_4CF_3\cdot \xrightarrow{C_2H_5\cdot} \underline{C_2H_5CF_3} + C_2H_4$$

$$C_2H_4CF_3\cdot \xrightarrow{C_2H_5CHO} \underline{C_2H_5CF_3} + C_2H_5CO\cdot$$

Recently it has been shown that the addition of $CF_3\cdot$ to ethylene occurs over 1,000 times more rapidly than

addition of $CH_3\cdot$ (61), while the C-H bond strength in CF_3H is likely to make disproportionation with alkyl radicals a more important mode of reaction for $CF_3\cdot$ than it is for $CH_3\cdot$. Since ethylene is formed by one of these reactions and removed by the other, the fluctuating values observed for the yield of ethylene relative to that of butane are explained. The observed high, temperature dependent, values calculated for the cross-combination ratio may also be explained in terms of the formation of additional $C_2H_5CF_3$ by the reactions indicated.

As a test of this mechanism HFA was photolysed in the presence of ethane, ethyl radicals being formed by abstraction. Similar results were observed. It seems probable that similar complications occur whenever alkyl radicals (other than methyl) react with perfluoroalkyl radicals, invalidating the reported cross-combination and disproportionation/combination ratios for such systems.

CHAPTER 8

POLARITY EFFECTS

In previous chapters the effect of dipole-dipole interactions upon the kinetics of hydrogen atom abstraction has been discussed. In Table 49 Arrhenius parameters for the reaction

$$CF_3\cdot + RH \longrightarrow CF_3H + R\cdot$$

are listed in order of decreasing electronegativity of R. While A increases steadily by a factor of almost 1000 on going from methanol to trimethylsilane, there is no such systematic variation in E.

TABLE 49

RH	Log A	E	
←			
MeOH	9·5	3·2	This Work
$MeNH_2$	9·9	4·4	" "
Me_2NH	10·5	3·3	" "
SH_2	11·2	1·2	Kale and Timmons
Me_3CH	11·3	5·3	See Table 23
SiH_4	11·9	5·1	This Work
Me_3SiH	12·3	5·5	" "
→			

E is in kcal/mole, A in $mole^{-1}cm^3sec^{-1}$.

The hydrogen abstracted is shown on the right of the formula

It will be observed that the A-factor reported by Kale and Timmons (71) for the reaction

$$CF_3\cdot + H_2S \longrightarrow CF_3H + SH\cdot$$

fits smoothly into this series. A similar trend is observed for reactions of the type:-

$$CF_3\cdot + RCH_3 \longrightarrow CF_3H + RCH_2\cdot$$

Here it should be possible to observe the effects of dipole interactions more specifically, since in each case the hydrogen abstracted is bonded to a saturated carbon atom. In Fig. 41 Log A is plotted against the dipole moment of RCH_3. (In the case of trimethylamine the component of the dipole moment along each N-Me bond is taken so that a realistic comparison may be made with methanol and methylamine.)

TABLE 40

	$SiMe_4$	NMe_3	$MeNH_2$	MeOH
Log A	12·0	11·8	10·7	10·0
E	7·6	4·5	4·2	4·7
μ	0	0·67	1·26	1·70

E is in kcal/mole, A in $mole^{-1}cm^3sec^{-1}$, μ in e.s.u. x 10^{18}.

Again there appears to be a marked lowering of A-factor for $CF_3\cdot$ attack on possible sites, but no systematic variation in activation energy.

$$\overset{\delta-}{R}\text{ - }\overset{\delta+}{CH_3} \qquad \overset{\delta+}{CF_3}$$

In previous chapters this effect has been attributed to relatively long-range electrostatic forces deflecting in incoming $CF_3\cdot$ radical away from +ve. molecular sites, and towards -ve. sites. Such an explanation is, of course, tenable only if $CF_3\cdot$ possesses a dipole moment, which would not

VARIATION WITH DIPOLE MOMENT
OF RCH_3 OF LOG A FOR THE REACTION:- $RCH_3 + CF_3\cdot \longrightarrow RCH_2\cdot + CF_3H$

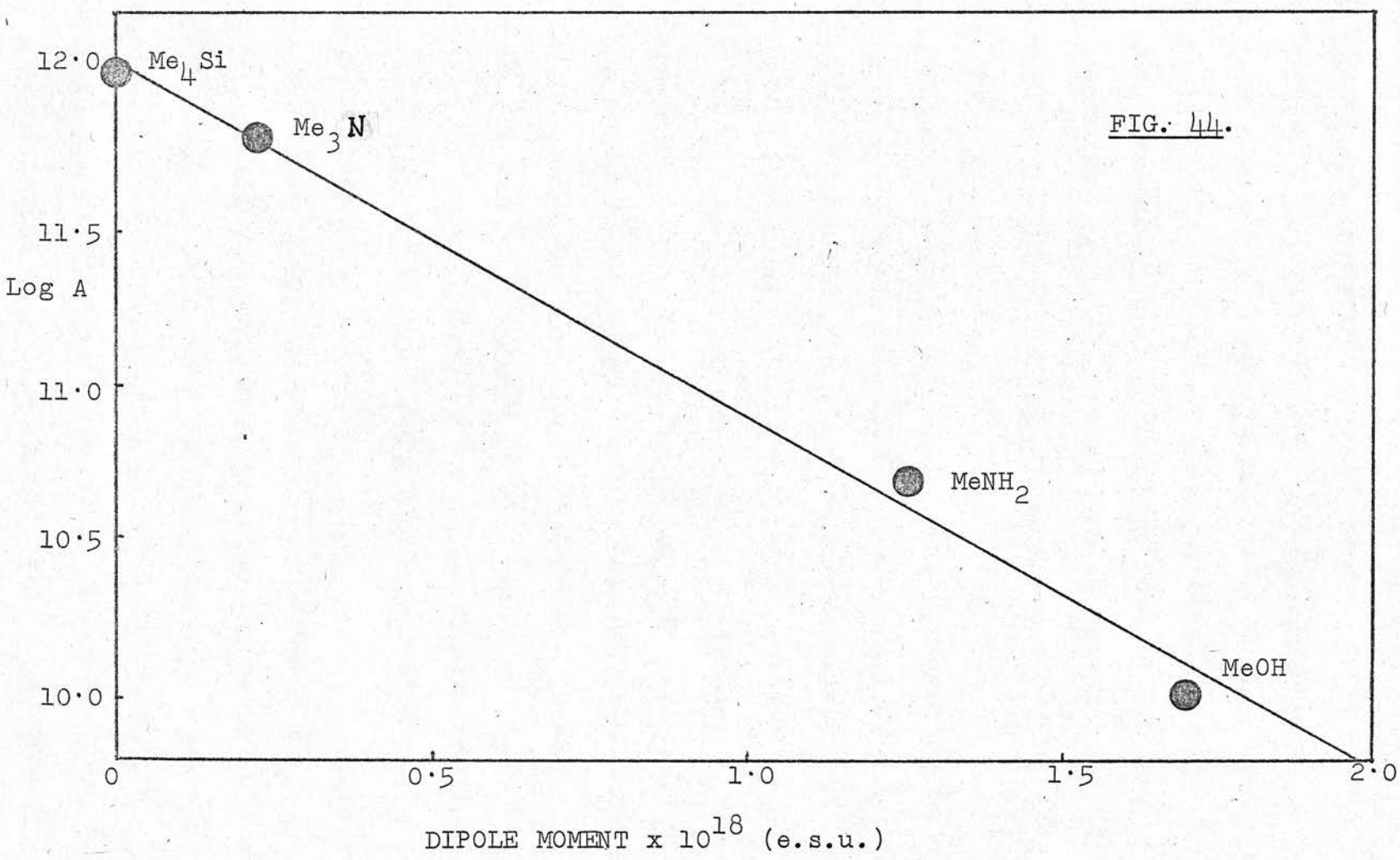


FIG. 44.

be the case if the radical exists preferentially in a planar configuration. Theoretical predictions from electron orbital calculations (153) suggest a non-planar structure, and this is confirmed by E.S.R. studies (134), which show that at 85°K the radical is virtually tetrahedral. While this cannot be taken as conclusive proof that the same configuration will be adopted at the considerably higher temperatures involved in gas-phase kinetic studies, the balance of probabilities appears strongly to favour a planar structure.

While it is generally agreed that hydrogen atoms in positive sites show enhanced resistance to $CF_3\cdot$ attack, the origin of this effect has not been conclusively established. The results obtained in the present work suggest that dipole-dipole interactions lower the probability of collision, and hence the A-factor, but that the forces involved are small in comparison with the activation energy for abstraction, $E_{CH_3} - E_{CF_3}$ being close to 3 kcal/mole for each of the substrates studied. Other workers however, have reported low or even negative values for this difference in activation energies for abstraction from polar molecules.

The first three compounds listed in Table 51 trifluoroacetaldehyde, dimethylformamide and methyl formate all involve abstraction from the CHO group. If the mechanism proposed in Chapter 7 is valid, then abnormal activation energies are to be expected, since the mode of attack is different from that involved in normal hydrogen abstractions.

The complications mentioned in Chapter 6 appear to invalidate the parameters reported for hydrogen abstraction from ammonia by $CF_3\cdot$, probably due to the formation in the initial abstraction process of a small radical with unshared electron pairs available for bonding. It seems likely that the conflicting kinetic data reported for $CF_3\cdot$ attack on hydrogen sulphide may result from similar complications. Until a fuller investigation of these two systems has been carried out, it would be unwise to attack too much significance to the parameters reported.

TABLE 51

	METHYL RADICALS			TRIFLUOROMETHYL			ΔE
	E	Log A	Ref	E	Log A	Ref	
Me_2NCHO	8·3	11·4	129	7·4	12·1	135	0·9
CF_3CHO	8·7	12·1	p	8·6	11·9	a	0·1
MeOCHO	9·9	11·2	84	8·7	11·4	84	1·2
H_2S	3·1	11·8	c	4·2	11·8	116	-1·1
NH_3	9·8	10·8	82	8·3	10·6	119	1·5
HCl	4·4		b	5·3	11·4	116	-0·9

E is in kcal/mole, A in $mole^{-1}cm^3sec^{-1}$.

a - Average of results from Ref. 17 and this work.

b - Calculated thermochemically from results of Ref. 138.

c - Average of results from Refs. 136 and 137.

p - This work.

The remaining parameters given in Table 51, (for the reaction $CF_3\cdot + HCl \longrightarrow CF_3H + Cl\cdot$) are in good agreement with those reported by Whittle, who with various

co-workers has studied hydrogen abstraction by trifluoromethyl radicals from a large number of halogen-containing compounds. The results of this work are summarised in Table 52.

TABLE 52

	E	Log A	Log k_{164}	Ref.
HCl	5·1	11·2	8·6	139
HBr	2·9	11·8	10·3	139
HI	0·5	11·7	11·4	140
CH_3F	11·2	12·1	6·5	49
CH_3Cl	10·6	12·1	6·8	11
CH_3Br	10·4	12·0	6·8	11
CH_3I	7·5	10·6	6·8	11
CH_2F_2	11·2	11·9	6·3	49
CH_2Cl_2	7·6	11·2	7·4	66
$CHCl_3$	6·6	11·0	7·7	66
CH_3CF_3	15·8	12·9	5·0	49
CF_2HCF_3	11·5	11·3	5·5	49
CF_2HCF_2H	12·4	12·0	5·8	49
(CH_3CH_3)	8·4	11·7	7·5	49

F is in kcal/mole, A and k_{164} in $mole^{-1}cm^3sec^{-1}$.

Although k_{164} for abstraction from related compounds decreases with increasing polarity, there is no suggestion

of the variations in A-factor found in the present work. Indeed, the highest A-factor reported is for the substrate in which hydrogen occupies the most strongly positive site:

CF_3CH_3 $\longleftarrow+$ $\cdot CF_3$ $+\longrightarrow$

The reason for this discrepancy is not clear.

ABSTRACTION OF HYDROGEN FROM FLUOROFORM

As outlined in Chapter 1,it is possible to calculate Arrhenius parameters for the reaction

$$R\cdot + CF_3H \longrightarrow RH + CF_3\cdot$$

from the measured parameters for hydrogen abstraction from RH by $CF_3\cdot$. In Table 53 calculated Arrhenius parameters are listed for hydrogen abstraction from methane and fluoroform by $CH_3O\cdot$ and $CH_3NH\cdot$ radicals, together with the corresponding parameters for the highly reactive phenyl radical, and the considerably less reactive bromine atom.

TABLE 53

		Fluoroform			Methane		
R	D(R-H)	E	Log A	Ref	E	Log A	Ref
$C_6H_5\cdot$	112	5·2	9·9	147	7·5	10·9	147
$CH_3O\cdot$	102	7·2	9·5	r	8·8	11·1	r
$CH_3NH\cdot$	93	18·4	9·9	r	15·8	10·4	r
$Br\cdot$	87	22·0	13·0	148	18·2	13·2	149

E and D are in kcal/mole, A in $mole^{-1}cm^3sec^{-1}$.

r - Calculated from reverse parameters.

The following thermochemical data were used in calculating the reverse parameters.

BOND DISSOCIATION ENERGIES (kcal/mole)		Ref.
$D(CH_3\text{-}H)$	= 104	141
$D(CF_3\text{-}H)$	= 106	141
$D(CH_3O\text{-}H)$	= 102	142
$D(CH_3NH\text{-}H)$	= 93	143
ALSO		
$D(C_6H_5\text{-}H)$	= 112	3
D(Br-H)	= 87	4

ENTROPIES OF FORMATION (cal $deg^{-1}mole^{-1}$)			Ref.
(CH_4)	:	44·5	143
$(CH_3\cdot)$	:	46·0	143
(CF_3H)	:	62·0	143
$(CF_3\cdot)$	:	60·7	143
(CH_3OH)	:	56·5	145
$(CH_3O\cdot)$	:	55	144
(CH_3NH_2)	:	57·7	146
$(CH_3NH\cdot)$	:	56·3	110

For the reaction $CF_3\cdot + RH \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CF_3H + R\cdot$

$$\Delta H = E_f - E_r = D(CF_3\text{-}H) - D(R\text{-}H) = 106 - D(R\text{-}H) \text{ kcal/mole}$$

$$\Delta S = \left\{ S^\circ_{298}(CF_3H) - S^\circ_{298}(RH) \right\} + \left\{ S^\circ_{298}(R\cdot) - S^\circ_{298}(CF_3\cdot) \right\}$$

$$= 1\cdot3 - \left\{ S^\circ_{298}(RH) - S^\circ_{298}(R\cdot) \right\} \quad \text{cal. deg}^{-1}\text{mole}^{-1}.$$

Similarly for $CH_3\cdot + RH \rightleftharpoons CH_4 + R\cdot$

$$\Delta H = \underline{104 - D(R\text{-}H)} \text{ and } \Delta S = \underline{-1\cdot5 - \left\{ S^\circ_{298}(RH) - S^\circ_{298}(R\cdot) \right\}}$$

While rate constants calculated in this way are probably not accurate to better than an order of magnitude, nonetheless they do provide a guide to the reactivities of the polar methoxy and methylamino radicals with polar and non-polar hydrogen substrates.

It will be noted that for both substrates the activation energy for abstraction decreases with increasing strength of the R-H bond formed.

QUANTUM MECHANICAL TUNNELLING.

The Arrhenius parameters derived for hydrogen and deuterium atom abstraction by $CF_3\cdot$ from the methyl positions in CH_3OH/CD_3OH and CH_3NH_2/CD_3NH_2 suggest that tunnelling may be occurring to an appreciable extent. In both cases $E_D - E_H = 1{\cdot}9$ kcal/mole as against a zero-point energy difference of 1·2 kcal/mole, while the ratio A_H/A_D is less than 1 in both cases. Similar results have been obtained by other workers as shown in Table 54.

TABLE 54.

	E	Log A	E_D-E_H	Ref.
$CD_3OH + CH_3\cdot \longrightarrow \cdot CD_2OH + CH_3D$	11·9	11·3	1·9	114
$CH_3OH + CH_3\cdot \longrightarrow \cdot CH_2OH + CH_4$	10·0	11·3		
t-BuD + $CD_3\cdot \longrightarrow$ t-Bu· + CD_4	9·7	11·5	1·6	111
t-BuH + $CD_3\cdot \longrightarrow$ t-Bu· + CD_3H	8·1	11·4		
$CD_3H + CF_3\cdot \longrightarrow CD_2H\cdot + CF_3D$	12·7	11·3	2·2	150
$CD_3H + CF_3\cdot \longrightarrow CD_3\cdot + CF_3H$	10·5	11·0		
$CD_3OH + CF_3\cdot \longrightarrow \cdot CD_2OH + CF_3D$	6·6	10·2	1·9	This work
$CH_3OH + CF_3\cdot \longrightarrow \cdot CH_2OH + CF_3H$	4·7	10·0		
$CD_3NH_2 + CF_3\cdot \longrightarrow \cdot CD_2NH_2 + CF_3D$	6·1	11·0	1·9	This work
$CH_3NH_2 + CF_3\cdot \longrightarrow \cdot CH_2NH_2 + CF_3H$	4·2	10·7		

E is in kcal/mole, A in $mole^{-1}cm^3sec^{-1}$.

There is no evidence however, that tunnelling is important in the case of abstraction from the amino group in $(CH_3)_2NH$

and $(CH_3)_2ND$, the difference in activation energies being close to the zero-point energy difference of 1·3 kcal/mole. This is in accord with the findings of Gray and his co-workers for systems in which N-H and N-D bonds are broken by methyl radical attack. (81, 83, 122)

PERFLUOROALDEHYDES AS RADICAL SOURCES

As was shown in Chapter 7, the reaction

$$R_fCHO + h\nu \longrightarrow R_fH + CO$$

represents an important mode of photodecomposition of perfluoroaldehydes. Reported rate constants for the reaction

$$R_fCHO + R_f\cdot \longrightarrow R_fH + R_fCO\cdot$$

calculated on the assumption that this is the only source of R_fH are therefore likely to be seriously in error. The use of perfluoroaldehydes as radical sources for hydrogen abstraction from other substrates must also lead to high apparent rate constants for the reaction

$$R_f\cdot + RH \longrightarrow R_fH + R\cdot$$

If the rate of this reaction is sufficiently great, however, the intramolecular contribution to RH formation may become unimportant (124). In consequence perfluoroaldehydes are of use for hydrogen abstraction reactions only when the hydrogen atom in the substrate molecule is extremely reactive.

REACTIONS OF PERFLUOROALKYL RADICALS WITH ALKYL RADICALS

As mentioned in Chapter 1, cross-combination ratios are normally independent of temperature and close to 2. High, temperature-dependent cross-combination ratios have

been reported for a number of alkyl/perfluoroalkyl radical reactions as shown in Table 55.

TABLE 55

RADICALS		Φ	Ref.
$CH_3\cdot$	$C_2H_5\cdot$	2·0	126
$CH_3\cdot$	$i\text{-}C_3H_7\cdot$	2·0	127
$n\text{-}C_3H_7$	$n\text{-}C_4H_9\cdot$	2·0	151
Δ.	Allyl	2·0	152
$CH_3\cdot$	$CF_3\cdot$	2·0	38
$CF_3\cdot$	$C_2F_5\cdot$	1·95	This work
		2·08	123
$CF_3\cdot$	$n\text{-}C_3F_7\cdot$	1·8	54
$CH_3\cdot$	$n\text{-}C_3F_7\cdot$	0·74 exp(1440/RT)	16
$C_2H_5\cdot$	$C_2F_5\cdot$	4·7 exp (-750/RT)	51
$C_2H_5\cdot$	$n\text{-}C_3F_7\cdot$	2·8 exp (-1900/RT)	50
		3·2	52

The value reported for $CH_3\cdot$ and $n\text{-}C_3F_7\cdot$ was derived by Pritchard and his co-workers, who photolysed mixtures of acetone and perfluorobutyraldehyde (approx. 3:1), and analysed for C_2H_6, $CH_3C_3F_7$ and C_6F_{14}. Examination of published data for this system shows that the percentage decomposition of the aldehyde varied systematically from about 7% at low temperatures to around 90% at the top of the temperature range used (300-580°K). In view of the high extent of reaction, it seems possible that at high temperatures secondary reactions such as

$$CH_3\cdot + CH_3C_3F_7 \longrightarrow CH_4 + \cdot CH_2C_3F_7$$

may have affected the cross-combination ratio. Under these

circumstances it would seem unwise to regard the reported temperature dependence as conclusively established.

The temperature dependence observed for combination of $C_2H_5\cdot$ with perfluoroalkyl radicals, however, is in accord with results obtained in the present work for reactions of $CF_3\cdot$ with n-$C_4H_9\cdot$, $C_6H_{11}\cdot$ and $C_2H_5\cdot$ (Chapters 3 and 7), and may be explained in terms of the following reactions:-

$$\begin{array}{ccc} C_2H_5\cdot + R_f & \xrightarrow{k_d} & C_2H_4 + R_fH \\ \downarrow k_c & & R_f\cdot \downarrow k_b \\ C_2H_5R_f & \xleftarrow[RH]{k_a} & C_2H_4R_f\cdot \end{array}$$

Thus the cross-combination product $C_2H_5R_f$ is also formed by an alternative route, leading to a high value of Φ. Since both k_b and k_a will be temperature dependent, the observed increase in Φ at high temperatures is to be expected. A similar situation must exist for the combination of alkyl radicals. However, since k_b for alkyl radical addition to olefins is very much lower than for perfluoroalkyl radicals (61), the effect of this process will normally be negligible. It seems likely that reported disproportionation/combination ratios for perfluoroalkyl radicals with ethyl and higher alkyl radicals will be appreciably lowered by this reaction sequence.

As shown in Chapter 3, reported rate constants for hydrogen abstraction from alkanes by perfluoroalkyl radicals are likely to be high, due to the formation of additional R_fH by disproportionation. The presence of iodine (atomic and molecular) in the system appears to inhibit this reaction by removal of alkyl radicals.

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REACTIONS OF METHYL RADICALS WITH FLUOROALDEHYDES

Reactions of Methyl Radicals with Fluoroaldehydes

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Received 24th April 1967

The reactions of methyl radicals, generated by the thermal decomposition of di-tert butyl peroxide (DTBP), with CF_3CHO, C_2F_5CHO, and C_3F_7CHO have been studied and Arrhenius parameters for the following hydrogen atom abstraction reactions obtained:

	log A (mole^{-1} cm^3 sec^{-1})	E (k cal mole^{-1})
$CH_3+DTBP \rightarrow CH_4+C_8H_{17}O_2$	12·65	11·9
$CH_3+CF_3CHO \rightarrow CH_4+COCF_3$	12·10	8·7
$CH_3+C_2F_5CHO \rightarrow CH_4+COC_2F_5$	12·93	9·8
$CH_3+C_3F_7CHO \rightarrow CH_4+COC_3F_7$	13·19	10·3

The rate of hydrogen atom abstraction from the fluoroaldehydes appears to be independent of the size of the fluoroalkyl group. These results are compared with data for other reactions of the type: $CH_3+HCOX \rightarrow CH_4+COX$.

Comparison of the relative reactivities of methyl and trifluoromethyl radicals suggests that the nature of the substrate has considerable effect, with hydrocarbons methyl radicals being much less reactive, whereas with polar molecules or molecules containing a weak X—H bond, both radicals react by hydrogen-atom abstraction at similar rates.

Studies of hydrogen-atom abstraction by methyl radicals from molecules of the type HCOX are of interest since the abstraction of the formyl hydrogen atom (reaction (1)),

$$CH_3+HCOX \rightarrow CH_4+COX \qquad (1)$$

can be studied conveniently for different side groups and such reactions present the possibility that changes in the velocity constant and the Arrhenius parameters for the abstraction reaction can be correlated with the nature of the substituting group X.

Studies on aldehydes,[1] formates [2,3,4] and formamides [5] (i.e., X = R, OR and NR_2) have indicated that although the rate of hydrogen atom abstraction varies markedly between the three families, within a family the rate is independent of the size of the substituting group.

It is desirable to extend these studies to fluoroaldehydes in order to investigate the effect of large, strongly polar groups upon the reactivity of the formyl hydrogen atom and accordingly we have studied the reactions of methyl radicals with trifluoroacetaldehyde, pentafluoropropionaldehyde and heptafluoroaldehyde.

EXPERIMENTAL

MATERIALS

DI-tert-BUTYL PEROXIDE (Koch-Light Co.,) was dried and then distilled several times, the middle fractions being collected. It was stored on the vacuum line and was degassed before use.

TRIFLUOROACETALDEHYDE was prepared from the hydrate (Koch-Light Co.,); this was dropped slowly on to a stirred mixture of phosphorous pentoxide and concentrated sulphuric acid at 85-90°C. The gas evolved was collected in two traps, one at −80°C and one at −160°C. After bulb-to-bulb distillation on the vacuum line the aldehyde was stored at −196°C in a blackened blub. Comparison of the infra-red spectra with the literature spectrum [6] confirmed the identity of the product. PENTAFLUOROPROPIONALDEHYDE and HEPTAFLUOROBUTYRALDEHYDE were similarly prepared from their hydrates (Eastman Kodak).

APPARATUS AND PROCEDURE

The reaction cell was a spherical Pyrex vessel (184 cm^3) housed in an electric furnace, the temperature of which was controlled by a Bikini-Fenwall relay unit to ±0·2°C. The cell was connected by a short-side-arm to a conventional high-vacuum apparatus comprising cold traps, gas burette and Macleod gauge. Mixtures of the aldehyde and peroxide were made up in a large bulb, (using a dibutyl phthalate manometer for pressure measurements), before expansion into the cell. After reaction the contents of the reaction cell were expanded into a liquid-nitrogen-cooled trap. The non-condensable fraction was collected and measured in the gas burette before being analyzed mass-spectrometrically by an AEI Ltd. MS 10 mass spectrometer. This fraction contained methane and carbon monoxide. A further fraction volatile at −160°C was collected, measured and analyzed mass spectrometrically. This fraction comprised mainly ethane (plus a little carbon dioxide impurity from the aldehyde which could not be removed after prolonged pumping). With trifluoroacetaldehyde, for decomposition was greater than about 5 %, other peaks were observed in the mass spectrum of the −160° fraction. These correspond to m/e values of 31, 45, 51, 69 and 119 and presumably arise from products such as CF_3H, CF_3CH_3 and C_2F_6. In order to avoid substantial corrections for these products the aldehyde was decomposed to only a small extent (<3 %). No such contamination of the −160°C fraction was observed with the other aldehydes.

RESULTS

When methyl radicals are generated in the presence of di-tert-butyl peroxide (DTBP) and the fluoroaldehydes, methane is formed by hydrogen atom abstraction from both molecules. In order to correct for the methane formed from DTBP a study of this reaction was made.

HYDROGEN-ATOM ABSTRACTION FROM DTBP BY METHYL RADICALS

DTBP was thermally decomposed over the temperature range 127-171°C. Methane and ethane are formed by the following reactions:

$$CH_3 + DTBP \rightarrow CH_4 + C_8H_{17}O_2 \quad (2)$$

$$2CH_3 \rightarrow C_2H_6 \quad (3)$$

Under steady-state conditions the following rate relation may be deduced, where R_x is the rate of formation of X and (DTBP) is the mean concentration of the peroxide:

$$R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6}(DTBP) = k_2/k_3^{\frac{1}{2}}.$$

Using the value [7] of $10^{13.34}$ (mole^{-1} cm^3 sec^{-1}) for the velocity constant of combination of methyl radicals, our data, when analyzed by the method of least-mean-squares, are expressed by the equation:

$$\log k_2 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (12{\cdot}65 \pm 0{\cdot}18) - (11900 \pm 300)/2{\cdot}303RT$$

The error limits quoted in this paper are the standard deviations. These Arrhenius parameters are in reasonable agreement with values of [8,9] 12·4 for $\log A_2$ and 11·7 and 14·5 ±2·5 kcal mole^{-1} for E_2.

TABLE 1.—HYDROGEN-ATOM ABSTRACTION FROM FLUOROALDEHYDES [HCOX] BY METHYL RADICALS.

temp (°K)	time (sec)	10^6 mole cm^{-3} [HCOX]	10^6 mole cm^{-3} [DTBP]	10^{12} mole cm^{-3} sec^{-1} CH_4	10^{12} mole cm^{-3} sec^{-1} C_2H_6	$R_{CH_4(abs)}/R_{\frac{1}{2}C_2H_6}$ [HCOX]
			TRIFLUOROACETALDEHYDE			
401·1	2500	0·59	0·28	2·23	0·75	4·21
401·5	480	0·49	0·24	2·45	1·27	4·33
405·2	750	0·53	0·40	5·02	2·81	5·43
409·7	600	0·69	0·35	7·86	4·34	5·29
415·1	1200	0·59	0·27	9·50	4·74	7·19
421·4	240	0·59	0·24	21·6	20·1	7·95
421·4	300	0·64	0·36	21·6	14·7	8·48
421·4	200	0·57	0·36	21·2	18·4	8·30
429·2	180	0·56	0·28	35·5	40·5	9·64
429·2	200	0·58	0·27	41·0	49·6	9·74
435·6	200	0·43	0·16	32·1	53·1	10·1
436·2	120	0·68	0·30	94·3	176·2	10·1
440·9	100	0·61	0·29	110·8	194·2	12·6
443·8	120	0·65	0·30	142·9	278·0	12·7
444·2	120	0·53	0·24	95·0	134·3	15·1
444·8	150	0·53	0·22	101·0	253·8	11·5
			PENTAFLUOROPROPIONALDEHYDE			
398·2	3600	0·22	0·12	0·91	$0·27_3$	7·94
398·2	1800	0·23	0·15	1·42	$0·51_0$	7·61
403·0	600	0·26	0·17	2·48	1·35	7·87
403·2	540	0·26	0·17	2·61	1·33	8·35
408·2	1200	0·19	0·13	2·33	1·41	10·2
408·2	900	0·25	0·19	4·49	2·20	12·6
413·0	480	0·23	0·11	4·74	2·47	13·0
413·2	480	0·30	0·16	6·33	2·69	12·4
418·4	420	0·30	0·19	11·4	7·11	14·0
423·2	480	0·26	0·16	14·2	12·8	15·1
428·2	420	0·22	0·15	15·6	14·1	18·0
433·6	480	0·19	0·10	16·6	19·1	20·0
438·2	240	0·18	$0·08_4$	18·5	19·3	23·0
438·2	300	0·17	0·10	22·0	26·5	23·7
			HEPTAFLUOROBUTYRALDEHYDE			
398·2	3600	0·31	0·14	1·15	$0·27_6$	6·85
398·4	1800	0·33	0·14	1·26	$0·34_1$	6·46
403·2	1620	0·26	0·17	1·51	$0·54_3$	7·60
403·2	1200	0·28	0·17	2·28	$0·86_7$	8·54
408·4	1200	0·25	0·12	2·48	$0·73_5$	11·6
408·2	1800	0·32	0·15	3·33	$0·96_7$	10·3
413·2	900	0·24	0·14	4·80	2·25	11·2
418·4	660	0·24	0·14	6·88	4·28	13·3
423·2	480	0·25	0·13	10·4	6·56	16·1
428·6	360	0·22	0·15	16·7	17·8	17·8
433·2	360	0·18	0·10	16·5	19·1	20·2
438·4	300	0·19	0·09	24·2	28·7	23·2

METHANE AND ETHANE FORMATION DURING THERMAL DECOMPOSITION OF DTBP IN PRESENCE OF R_fCHO.

When DTBP is thermally decomposed in the presence of the fluoroaldehydes the following reactions need to be added to the reaction scheme above to account for the methane formation:

$$CH_3 + CF_3CHO \rightarrow CH_4 + CF_3CO \quad (4)$$
$$CH_3 + C_2F_5CHO \rightarrow CH_4 + C_2F_5CO \quad (5)$$
$$CH_3 + C_3F_7CHO \rightarrow CH_4 + C_3F_7CO \quad (6)$$

If R_{CH_4} (4) is the steady rate of production of methane by reaction (4), obtained by subtracting from the total methane that part which comes from reaction (2), then the following rate relation applies:

$$R_{CH_4}(4)/R^{\frac{1}{2}}_{C_2H_6}(\text{ald}) = k_4/k^{\frac{1}{2}}_3.$$

where (ald) refers to the mean concentration of CF_3CHO. Similar rate relations can be obtained for the other aldehydes.

Our results for the three aldehydes are given in table 1. These data when treated by the method of least squares are represented by the following equations:

$$\log k_4 \text{ (mole}^{-1}\text{ cm}^3\text{ sec}^{-1}) = (12{\cdot}10 \pm 0{\cdot}16) - (8700 \pm 300)/2{\cdot}303RT,$$
$$\log k_5 \text{ (mole}^{-1}\text{ cm}^3\text{ sec}^{-1}) = (12{\cdot}93 \pm 0{\cdot}21) - (9800 \pm 300)/2{\cdot}303RT,$$
and
$$\log k_6 \text{ (mole}^{-1}\text{ cm}^3\text{ sec}^{-1}) = (13{\cdot}19 \pm 0{\cdot}18) - (10300 \pm 400)/2{\cdot}303RT.$$

There are no other Arrhenius parameters reported for any of these reactions. At 164°C the rate constants k_4, k_5 and k_6 have values of $10^{7{\cdot}8}$, $10^{8{\cdot}0}$ and $10^{8{\cdot}0}$ respectively (in mole^{-1} cm^{3}sec^{-1}) and so within experimental error are identical.

DISCUSSION

HYDROGEN ATOM ABSTRACTION FROM R_fCHO

The similarity of the rate constants for hydrogen atom abstraction from the three aldehydes indicates that all of the formyl hydrogen atoms are similarly reactive and that the size of the substituting group does not influence the reactivity of the formyl

TABLE 2.—HYDROGEN-ATOM ABSTRACTION BY METHYL RADICALS FROM HCOX

$$CH_3 + HCOX \rightarrow CH_4 + COX$$

X	mole^{-1} cm^3 sec^{-1} log A	kcal mole^{-1} E	mole^{-1} cm^3 sec^{-1} log k (164°)	ref.
CF_3	12·1	8·7	7·8	this work
C_2F_5	12·9	9·8	8·0	this work
C_3F_7	13·2	10·3	8·0	this work
CH_3O	10·7	8·6	6·4	2
C_2H_5O	10·5	8·2	6·4	3
C_3H_7O	10·1	7·3	6·4	4
NH_2	10·5	6·6	7·2	5
$NHCH_3$	10·9	7·6	7·1	5
$N(CH_3)_2$	11·4	8·3	7·2	5
CH_3	11·9	7·6	8·1	1
C_2H_5	12·0	7·5	8·2	1
C_3H_7	11·8	7·3	8·2	1

hydrogen. This is in general accord with the results reported for the aldehydes,[1] formates [2-4] and formamides.[5]

In table 2 we have compared Arrhenius parameter and rate constant data for hydrogen atom abstraction by methyl radicals from substrates of the type HCOX.

Although comparison of the molecules X = R, NR_2 and OR would suggest that the reaction rate decreased as the electronegativity of the side group increased, where X = R_f the trend is not sustained and the reactivity of the fluoroaldehydes is only slightly less than that of the aldehydes. This suggests that the effect of fluorine atoms being substituted for hydrogen is to cause only slight deactivation of the hydrogen atom on the adjacent carbon atom.

The activation energies required for abstraction are appreciably larger for the fluoroaldehydes than for any of the other comparable substrates so that it might be predicted that $D(H—COR_f) > D(H—COX)$. Also, the pre-exponential factors are about 10 times larger than usually observed for reactions of this nature. For methyl radicals reacting with a variety of aldehydes the pre-exponential factors varied from $10^{11.9}$ to $10^{13.1}$, values appreciably larger than those usually found.[10] Since "normal" values were reported for the formates and formamides it suggests that these high values are a common property of the aldehydes.

The activation energies required for hydrogen-atom abstraction increase steadily as the side group gets larger. The increase is outside the experimental error and might indicate that the H—COR bond was increasing in strength although the similarity in rate constants is evidence against this. Birrell and Trotman-Dickenson [1] observed that branching in the alkyl group was accompanied by a small increase in the Arrhenius parameters for hydrogen atom abstraction.

COMPARISON OF REACTIVITY OF CH_3 AND CF_3 RADICALS

Pritchard *et al.*[11] have suggested, on the basis of the hydrogen-atom abstraction reactions of methyl and trifluoromethyl radicals with hydrocarbon substrates, that CF_3 radicals are considerably more reactive and that this difference in reactivity stems from activation energy differences of 3-4 kcal $mole^{-1}$ between the two radicals. In table 3 we show data for methane, ethane and n-butane which support this suggestion.

TABLE 3.—COMPARISON OF REACTIVITY OF CH_3 AND CF_3 RADICALS WITH VARIOUS SUBSTRATES

	CH_4	C_2H_6	C_4H_{10}	H_2S	CF_3CHO
E_{CH_3}	14·7	11·8	9·6	2·6	8·7
E_{CF_3}	10·3	7·5	5·3	3·9	8·2
ΔE	4·4	4·3	4·3	−1·3	0·5
log (A_{CH_3}/A_{CF_3})	0·13	0·53	0·44	−0·25	0·5
k_{CF_3}/k_{CH_3}(164°C)	118	42	50	0·4	0·7
ref.	13, 14	15, 14	15, 16	17, 18	12, this work

E in kcal $mole^{-1}$

In table 3 we have also included data for attack by CH_3 and CF_3 radicals on molecules which lose hydrogen atoms readily to methyl radicals. For some of these systems various values have been reported for the activation energies. We have taken values near the average of these values or for H_2S that we considered to be the " best " value.

For molecules such as H_2S and CF_3CHO, hydrogen-atom abstraction by CF_3 radicals occurs at a similar (possibly slightly slower) rate as that with methyl radicals, and there is little difference in either the activation energies or the A-factors. For these molecules it is likely that the strength of the bond being broken is about 90-95 kcal $mole^{-1}$, i.e., much weaker than the bond being formed, whereas for the hydrocarbons there is much less difference between the bonds broken and formed. These results

might be explained in terms that the C—H bond strength has declined in strength to the stage where there is no difference in activation energy required for the two radicals. It is possible, however, that it is the polarity of the molecules which is the important factor and for molecules such as H_2S, repulsion forces between the radical and the molecule are significant and the activation energy is increased compared to the values observed with non-polar molcules.

Pritchard *et al.*[11] have considered that the activation energy of 8·2 kcal mole^{-1} reported by Dodd and Smith [12] for the reaction:

$$CF_3HCOCF_3 \rightarrow CF_3H + COCF_3 \qquad (7)$$

to be improbably high, because an activation energy difference of *ca.* 3-4 kcal mole^{-1} for methyl and trifluoromethyl radicals attacking the same molecule would suggest an activation energy of *ca.* 12 kcal mole^{-1} for reaction (4). Comparison of Dodd and Smith's value for reaction (7) with our measured value for E_4 indicates that their value is probably accurate and is compatible with other hydrogen atom abstraction data from polar molecules by trifluoromethyl radicals.

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Reactions of Radicals Containing Fluorine

Part 1.—Hydrogen and Deuterium Atom Abstraction from Trideuteromethanol by Trifluoromethyl Radicals

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Received 1st August, 1967

The reactions of trifluoromethyl radicals with methanol and trideuteromethanol have been studied in the temperature range 84-162°C in order to determine the rate at which hydrogen and deuterium atom abstraction occurs. Over this temperature range, abstraction from the hydroxyl group is slightly favoured over abstraction from the methyl group. Substitution of deuterium for hydrogen alters the positional reactivity by an amount in accord with the zero-point energy difference.

Arrhenius parameters (based upon a value of $10^{13.34}$ mole^{-1} cm^3 sec^{-1} of the rate constant of combination of trifluoromethyl radicals) have been measured for the reactions:

	log A	E
$CF_3 + n\text{-}C_4H_{10} \rightarrow CF_3H + C_4H_9$	11·3	5·7
$CF_3 + CH_3OH \rightarrow CF_3H + (COH_3)$	9·9	3·7
$CF_3 + CD_3OH \rightarrow CF_3H + CD_3O$	9·5	3·2
$CF_3 + CD_3OH \rightarrow CF_3D + CD_2OH$	10·2	6·6
$CF_3 + CH_3OH \rightarrow CF_3H + CH_2OH$	10·0	4·7

and have been calculated for

$CH_3O + CF_3H \rightarrow CH_3OH + CF_3$	9·5	7·7

(units of A mole^{-1} cm^3 sec^{-1} and E kcal mole^{-1}).

The reactions of the lower fluoroalkyl radicals with hydrocarbons have received much attention [1] and it has been suggested [2] that, for hydrogen atom abstraction reactions, the activation energies required are *ca.* 3 kcal mole^{-1} lower and the reaction rates much higher for the reactions involving fluoroalkyl radicals than for the alkyl radicals. There are few data [3-5] reported for the hydrogen atom abstraction reactions of fluoroalkyl radicals with polar molecules; however, these suggest that there are much smaller differences between both the activation energies and the reaction rate constants for such reactions and the values observed for alkyl radicals. It is not clear to what extents the polarity of the substrate molecule or the strength of the bond being broken determine the reaction rates in such cases. A molecule such as methanol should provide information in this respect, and by using CD_3OH the relative reactivities of the hydrogen atoms attached to the carbon and oxygen atoms may be evaluated. Carlton *et al.*[6] have reported data for this reaction; however, our preliminary experiments showed completely different rates of attack on the CD_3OH from their results and accordingly we carried out an investigation of the reaction of trifluoromethyl radicals with methanol and trideuteromethanol.

EXPERIMENTAL

Hexafluoroacetone (HFA) and hexafluoroazomethane (HFAM) are the two sources normally used to generate trifluoromethyl radicals. However, because of the reactivity of the carbonyl group in HFA with molecules such as methanol, methyl mercaptan and

methylamine, it cannot be used as a radical source with such substrates. HFAM is a photochemical source of trifluoromethyl radicals but suffers from the disadvantage that these radicals react extremely readily by the addition to the parent molecule.

Trifluoromethyl iodide (TFMI) is a good photolytic source of CF_3 radicals. It does not react with methanol and accordingly we have used this as our radical source.

MATERIALS

TRIFLUOROMETHYL IODIDE (Pierce Chemical Co.,) contained small amounts of fluoroform, hexafluoroethane and carbon dioxide. These were removed by low-temperature distillation at $-130°C$ in a vacuum line.

HEXAFLUOROACETONE (Dupont Co.,) contained fluoroform, hexafluoroethane, tetrafluoroethylene and carbon dioxide. These were removed as stated above.

TRIDEUTEROMETHANOL (Merck Sharp and Dohme,) METHANOL and n-BUTANE were throughly degassed and stored on the vacuum line.

PROCEDURE

The reaction cell was a quartz cylinder (volume 218 cm^3) which was housed in a heavy aluminium block furnace fitted with quartz side windows. A modified Bikini-Fenwal relay unit controlled the furnace temperature to better than $\pm 0{\cdot}2°C$. The reaction cell was fitted with a Teflon stopcock and metal valves were used in the analytical system. The light source was an Hanovia 220 W mercury lamp and a parallel beam from the full arc was used.

Reaction mixtures of the radical source and the substrate were made up by making use of a butyl phthalate manometer. Within our experimental error no changes in pressures were observed in mixing TFMI with methanol or n-butane or HFA with n-butane. On mixing HFA and methanol a considerable pressure decrease was observed and a white crystalline solid was formed.

After reaction the contents of the cell were expanded into the analytical train and collected in a liquid-nitrogen trap. After the removal of carbon monoxide (when HFA was used) by pumping, the contents of the trap were transferred quantitatively by a Toepler pump to the injection system of the gas chromatography apparatus. The analysis of C_2F_6 and CF_3H was performed on a 3 m column of silica gel at 50°C using hydrogen as a carrier gas and a Gow-Mac thermistor detector. In experiments involving CD_3OH, CF_3H and CF_3D were eluted from the column together and were trapped in a U-tube at $-196°C$. They were then analyzed mass-spectrometrically using an AEI Ltd. MS 10 mass spectrometer. The sensitivities of CF_3H and CF_3D were assumed to be the same and the peaks at m/e equal to 51 and 52 were used in the analysis, a correction being applied to the 52 peak for the contribution from $^{13}CF_2H^+$.

RESULTS

As a check on our experimental and analytical technique we studied the reaction of n-butane with CF_3 radicals using the photolyses of HFA and TFMI to generate the radicals. This reaction was chosen since it has been studied by other workers.

HYDROGEN ATOM ABSTRACTION FROM n-BUTANE

USING HFA.—When CF_3 radicals are generated in the presence of n-butane, fluoroform and hexafluoroethane are formed by the following reactions:

$$CF_3 + C_4H_{10} \xrightarrow{1} CF_3H + C_4H_9$$

$$2CF_3 \xrightarrow{2} C_2F_6$$

Our data, given in table 1, are represented by the equation

$$\log k_1(\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = (11{\cdot}77 \pm 0{\cdot}24) - (6190 \pm 430)/2{\cdot}303RT,$$

where the error limits are the standard deviations of a least-mean-squares computer treatment and the rate constant of combination of trifluoromethyl radicals is assumed[7] to be $10^{13.34}$ (mole^{-1} cm^3 sec^{-1}). Other values reported,[8, 9] for the Arrhenius parameters of reaction (1) are 11·15 (mole^{-1} cm^3 sec^{-1}) and 5·1 (kcal mole^{-1}) and 11·46 and 5·3.

TABLE 1.—HYDROGEN ATOM ABSTRACTION FROM n-BUTANE BY TRIFLUOROMETHYL RADICALS (using HFA).

T°K	t (sec)	C_4H_{10}	HFA	CF_3H	C_2F_6	$k_1/k_2^{\frac{1}{2}}$
357·1	45	0·391	1·44	58·7	50·5	21·1
357·1	45	0·586	1·66	65·9	29·1	20·9
357·1	180	0·506	1·86	64·9	38·1	20·8
370·2	45	1·65	0·747	86·3	4·95	23·5
370·2	180	1·62	0·735	82·1	4·83	23·0
370·3	90	0·423	1·04	100·1	29·8	43·4
370·5	90	0·724	0·766	99·2	21·2	29·8
384·5	60	0·415	1·89	117·1	50·1	39·9
400·0	45	0·551	1·56	177·9	39·6	51·3
400·0	60	0·276	1·26	120·4	67·4	53·2
416·6	45	0·980	0·977	226·6	10·1	72·7
416·6	90	1·27	0·57	175·8	5·10	61·4
434·6	45	0·371	1·69	315·0	63·8	106·3
434·8	45	0·318	1·17	262·5	71·0	98·0
434·9	60	0·450	1·27	279·1	39·7	98·4

C_4H_{10} and HFA in 10^{-6} mole cm^{-3}; CF_3H and C_2F_6 in 10^{-12} mole cm^{-3} sec^{-1}.

USING TFMI.—When TFMI was used as the radical source over the same temperature and concentration ranges, values for k_1 were obtained which were consistently lower than the values obtained using the ketone as the radical source. Our data given in table 2 are expressed by

$$\log k_1 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (11{\cdot}31 \pm 0{\cdot}16) - (5740 \pm 280)/2{\cdot}303RT.$$

TABLE 2.—HYDROGEN ATOM ABSTRACTION FROM n-BUTANE BY TRIFLUOROMETHYL RADICALS (using TFMI).

T°K	t (sec)	C_4H_{10}	TFMI	CF_3H	C_2F_6	$k_1/k_2^{\frac{1}{2}}$
357·1	450	0·419	1·58	7·78	1·27	16·5
357·2	900	0·479	1·71	6·56	1·05	13·4
370·3	450	0·162	1·99	5·80	4·31	17·3
370·3	450	0·722	1·48	15·1	1·55	16·8
370·5	450	0·841	0·816	17·0	1·22	18·2
384·6	450	0·439	1·65	12·5	1·22	25·7
400·2	450	0·463	1·65	14·7	1·07	30·7
416·4	450	0·145	1·79	11·2	3·56	41·4
416·6	180	0·775	0·752	41·9	1·75	40·9
416·7	200	0·628	1·29	34·5	1·75	41·6
434·8	300	0·410	1·54	30·3	1·41	62·3
434·9	450	0·315	1·13	18·4	0·80$_4$	65·1

C_4H_{10} and TFMI in 10^{-6} mole cm^{-3}; CF_3H and C_2F_6 in 10^{-12} mole cm^{-3} sec^{-1}.

Although our two equations give values for k_1 which agree within the standard deviation limits, comparison of the final columns of tables 1 and 2 shows the rate constant ratio ($k_1/k_2^{\frac{1}{2}}$) to be more nearly constant over a wide concentration range for TFMI+C_4H_{10} mixtures than for HFA+C_4H_{10} mixtures. This suggests an

additional reaction leading to the formation of CF_3H in the latter system. Examination of the reaction products for this system showed that appreciable yields of butene-1 and cis- and trans-butene 2 were formed, presumably by the reactions:

$$CF_3 + CH_3CHCH_2CH_3 \xrightarrow{3} CF_3H + CH_3CH = CHCH_3$$

$$CF_3 + CH_3CHCH_2CH_3 \xrightarrow{4} CF_3H + CH_2 = CHCH_2CH_3$$

$$CF_3 + CH_2CH_2CH_2CH_3 \xrightarrow{5} CF_3H + CH_2 = CH_2{=}CHCH_2CH_3.$$

Participation of these reactions would lead to an apparent excess of CF_3H formation by reaction (1).

When TFMI was the radical source butene formation was inhibited. Since iodine atoms are generated in the primary photolytic act they are present (with molecular iodine) in high concentrations in the reaction system and can readily react with the hydrocarbon radicals produced in the initial abstraction reaction (1), i.e.

$$I + C_4H_0 \xrightarrow{6} C_4H_9I\,.$$

The occurrence of such a reaction would prevent CF_3H formation by reactions (3)-(5). We consider it unlikely that there is any contribution to CF_3H formation by reactions (7) and (8) because of the inhibition of butene formation when TFMI + C_4H_{10} mixtures are photolyzed:

$$I + C_4H_9 \xrightarrow{7} HI + C_4H_8$$

$$CF_3 + HI \xrightarrow{8} CF_3H + I.$$

The A-factor obtained using HFA is higher than that obtained using TFMI. Benson [10] has suggested that the occurrence of secondary reactions between the generating radical and the product radical would lead to a low A-factor. It appears from our data that the A-factor is not noticeably affected by such a reaction. Unpublished results obtained in this laboratory using cyclohexane show the same behaviour.

CF_3H, CF_3D AND C_2F_6 FORMATION IN PRESENCE OF CH_3OH

When CF_3 radicals (from TFMI) are produced in the presence of trideuteromethanol the products observed and analyzed quantitatively were CF_3H, CF_3D and C_2F_6. Small quantities of CD_4 and CD_3H were also observed among the permanent gas fraction. Their formation is accounted for by the following reaction scheme:

$$CF_3 + CD_3OH \xrightarrow{9} CF_3H + CD_3O$$

$$\xrightarrow{10} CF_3D + CD_2OH$$

The following steady-state relationships apply:

$$R_{CF_3H}/R^{\frac{1}{2}}_{C_2F_6}[CD_3OH] = k_9/k_2^{\frac{1}{2}} \quad \text{and} \quad R_{CF_3D}/R^{\frac{1}{2}}_{C_2F_6}[CD_3OH] = k_{10}/k_2^{\frac{1}{2}},$$

where $[CD_3OH]$ denotes the concentration of trideuteromethanol. Our results are shown in table 3 and, when treated by the method of least-mean-squares, are represented by the equations (using $k_2 = 10^{13.34}$):

$$\log k_9 \text{ (mole}^{-1}\text{ cm}^3\text{ sec}^{-1}) = (9{\cdot}48 \pm 0{\cdot}35) - (3240 \pm 630)/2{\cdot}303RT,$$

and

$$\log k_{10} \text{ (mole}^{-1}\text{ cm}^3\text{ sec}^{-1}) = (10{\cdot}20 \pm 0{\cdot}23) - (6610 \pm 630)/2{\cdot}303RT.$$

TABLE 3.—HYDROGEN AND DEUTERIUM ATOM ABSTRACTION FROM CD_3OH BY TRIFLUOROMETHYL RADICALS

T°K	t (sec)	CD_3OH	TFMI	CF_3H	CF_3D	C_2F_6	A	B
357·1	1200	0·395	1·59	1·72	0·077	0·877	4·6	0·210
357·1	1500	0·291	1·57	1·69	0·076	0·711	6·9	0·311
357·1	1800	0·249	1·76	1·62	0·073	0·650	8·1	0·366
370·2	1200	0·182	1·29	1·35	0·071	0·730	8·6	0·458
384·5	1800	0·278	1·50	1·72	0·109	0·617	7·9	0·497
384·6	2400	0·210	1·45	1·73	0·019	0·458	12·1	0·769
400·0	1800	0·202	1·43	1·67	0·125	0·638	10·3	0·772
400·0	2500	0·335	1·35	2·24	0·168	0·356	11·2	0·838
416·6	1800	0·348	0·788	2·25	0·199	0·357	10·8	0·959
416·8	1800	0·237	0·953	2·28	0·202	0·483	15·5	1·38
434·8	450	0·222	1·54	3·61	0·382	1·64	12·7	1·34
434·8	2000	0·213	1·47	2·45	0·259	0·471	16·7	1·77

$A = R_{CF_3H}/R^{\frac{1}{2}}_{C_2F_6}$ (CD_3OH); $B = R_{CF_3D}/R^{\frac{1}{2}}_{C_2F_6}$ (CD_3OH);
CD_3OH and TFMI in 10^{-6} mole cm^{-3}; CF_3H, CF_3D and C_2F_6 in 10^{-12} mole cm^{-3} sec^{-1}.

The formation of CD_3H and CD_4 suggests that the following displacement reaction occurs,

$$CF_3 + CD_3OH \rightarrow CF_3OH + CD_3,$$

followed by

$$CD_3 + CD_3OH \rightarrow CD_3H + CD_3O$$
$$\rightarrow CD_4 + CD_2OH.$$

TABLE 4.—HYDROGEN ATOM ABSTRACTION FROM METHANOL BY TRIFLUOROMETHYL RADICALS

T°K	t (sec)	CH_3OH	TFMI	CF_3H	C_2F_6	$k_{11}/k^{\frac{1}{2}}_2$
356·8	1200	0·496	1·38	3·69	0·734	8·7
357·0	1200	0·285	1·655	2·36	0·867	8·9
357·1	1800	0·369	1·49	2·49	0·555	9·0
370·2	1800	0·193	1·72	1·90	0·723	11·6
370·2	1800	0·570	1·75	3·93	0·500	9·7
384·5	1200	0·363	1·47	3·72	0·689	12·3
384·9	1200	0·195	1·74	2·77	0·920	14·8
400·0	600	0·593	1·23	7·29	0·734	14·3
400·1	1200	0·619	1·29	6·51	0·520	14·6
400·3	1200	0·247	1·68	3·63	0·937	15·2
415·6	900	0·236	1·58	5·38	1·13	21·5
415·6	1800	0·240	1·60	4·67	0·792	21·9
416·2	200	0·230	0·99	6·95	3·51	16·1
416·4	600	0·381	1·03	6·32	0·937	17·1
416·6	600	0·334	1·03	7·47	1·00	22·3
416·6	600	0·340	1·04	7·20	0·826	23·3
434·1	240	0·386	1·07	11·7	1·81	22·7
435·0	600	0·397	1·10	9·31	0·848	25·1
435·0	600	0·229	1·56	6·01	1·09	25·1

CH_3OH and TFMI in 10^{-6} mole cm^{-3}; CF_3H and C_2F_6 in 10^{-12} mole cm^{-3} sec^{-1}.

CF_3H AND C_2F_6 FORMATION IN PRESENCE OF CH_3OH

When the reaction of CF_3 radicals is carried out in the presence of unlabelled methanol, the CF_3H formation reveals only the overall rate of hydrogen atom abstraction from the alcohol, i.e., reaction (11) represents the sum of the individual reactions

(12) and (13):

$$CF_3 + CH_3OH \xrightarrow{11} CF_3H + (H_3OC)$$
$$\xrightarrow{12} CF_3H + CH_3O$$
$$\xrightarrow{13} CF_3H + CH_2OH$$

The overall velocity constant k_{11} is given by the relation:

$$R_{CF_3H}/R^{\frac{1}{2}}_{C_2F_6}[CH_3OH] = k_{11}/k^{\frac{1}{2}}_2.$$

Our data are given in table 4 and are represented by the equation:

$$\log k_{11}\ (\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = (9{\cdot}92 \pm 0{\cdot}15) - (3740 \pm 270)/2{\cdot}303RT.$$

By making the assumption that $k_{12} = k_9$ (i.e., that there is no significant secondary isotope effect) we deduce the Arrhenius parameters for reaction (13). We find that

$$\log k_{13}\ (\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = 10{\cdot}0 - 4700/2{\cdot}303RT.$$

DISCUSSION

PRIMARY ISOTOPE EFFECTS IN CF_3 RADICAL ATTACK ON METHANOL

The results enable a primary isotope effect to be determined for the CD_3— and CH_3— groups in methanol. Comparison of k_{10} and k_{13} indicates that a hydrogen atom is abstracted more readily than is a deuterium atom. The ratio k_{13}/k_{10} varies with temperature having a value of 6·3 at 164°C. Comparison of the equations for reactions (10) and (13) indicate that, within experimental error, the pre-exponential factors are equal. The activation energy difference $E_{10} - E_{13}$ $(= E_D - E_H)$ is $1{\cdot}9 \pm 0{\cdot}6$ kcal mole^{-1}. Within this large experimental scatter this difference is equal to the zero-point energy (z.p.e.) difference corresponding to a single C—H and C—D stretching vibration, i.e., 1·2 kcal mole^{-1}.

Below we compare data for the primary isotope effect for methanol using methyl [11] and trifluoromethyl radicals.

radical	substrates	A_H/A_D	$-(E_H - E_D)$	$k_H/k_D(164°)$	z.p.e. diff.
CF_3	CD_3OH, CH_3OH	0·6	1·9	5·6	1·2
CH_3	CD_3OH, CH_3OH	0·6	1·1	6·3	1·2

HYDROGEN ATOM ABSTRACTION FROM METHANOL

A feature of our results for the reactions of CF_3 radicals with methanol is the low pre-exponential factor for the reaction involving breaking of the O—H bond, although the *A*-factor for breaking the C—H bond is about normal. Our data do not agree with those of Carlton *et al.* [6] These workers used hexafluoroazomethane as their radical source and a competitive technique involving infra-red analysis of the reaction mixture to follow the reaction. They report the ratio $[CF_3D]/[CF_3H]$ to have values varying from 1·08 at 107°C to 2·55 at 255°C. Our values vary from 0·05 at 84°C to 0·10 at 162°C. We have no explanation why these two sets of experimental data differ so considerably.

Since iodine atoms are present in the reaction system the following reaction sequence may contribute to the formation of CF_3H and CF_3D:

$$I + CD_3O \xrightarrow{14} DI + CD_2O$$
$$CF_3 + DI \xrightarrow{15} CF_3D + I$$
$$I + CD_2OH \xrightarrow{16} HI + CD_2O$$
$$CF_3 + HI \xrightarrow{17} CF_3H + I.$$

We consider it unlikely that reaction (15) or reaction (17) will occur so extensively as to explain the difference in $[CF_3D]/[CF_3H]$ ratios mentioned above, particularly since Whittle in his study [12] of the photo-bromination of methanol has suggested that bromine atoms abstract hydrogen from the methyl groups of methanol. Similar behaviour with iodine atoms would lead to " extra " CF_3D formation, so that our ratios (0·05 at 84°C) represent an upper limit to the rate $[CF_3D]/[CF_3H]$.

In addition, it is likely that any significant contribution of reactions (15) and (17) or the analogous reactions with CH_3OH would become apparent as variations in the appropriate rate constant ratios as the concentration ratio [alcohol]/[iodide] is altered. Tables 3 and 4 show no variation greater than to be expected on the basis of experimental deficiencies.

TABLE 5.—COMPARISON OF VELOCITY CONSTANTS AT 164°C AND ARRHENIUS PARAMETERS FOR ABSTRACTION FROM METHANOL BY CF_3 AND CH_3 RADICALS

reaction	log A ($mole^{-1}$ cm^3 sec^{-1})	E (kcal $mole^{-1}$)	log k (164°) ($mole^{-1}$ cm^3 sec^{-1})	ref.
(*a*) OVERALL				
$CF_3+CH_3OH\rightarrow CF_3H$	9·92	3·7	8·07	this work
$CF_3+CH_3OH\rightarrow CF_3H$	11·6	8·3	7·45	6
$CH_3+CH_3OH\rightarrow CH_4$	10·68	8·4	6·48	11
(*b*)CD_3OH				
$CF_3+CD_3OH\rightarrow CF_3D$	10·20	6·6	6·90	this work
$CF_3+CD_3OH\rightarrow CF_3H$	9·48	3·2	7·88	this work
$CF_3+CH_3OD\rightarrow CF_3H(+CH_2OD)$	11·6	8·3	7·45	6
$CF_3+CH_3OH\rightarrow CF_3H(+CH_3O)$	12·6	8·3	8·45	6
$CD_3+CD_3OH\rightarrow CD_4$	10·18	9·3	5·53	11
$CD_3+CD_3OH\rightarrow CD_3H$	10·46	9·0	5·96	11

In table 5 we have compared the Arrhenius parameters and velocity constants at 164°C (where 2·303 RT is 2000) for the CF_3 + methanol and CH_3 + methanol systems. It is clear that the trifluoromethyl radical abstracts hydrogen much more readily from both the C—H and O—H positions than does a methyl radical. With the methyl radical, at 164°C the CH_3 group is about 1·8 times as reactive as the OH group in losing an hydrogen atom by abstraction. When CF_3 is the abstracting radical the OH group is slightly more reactive (1·5 times) than the methyl group.

Deuterium atom abstraction from the alkyl group by trifluoromethyl radicals requires a lower activation energy (by 2·7 kcal $mole^{-1}$) than methyl radicals, although the pre-exponential factors for both reactions are similar. In addition, CF_3 radicals abstract about 30 times more readily than methyl radicals from the alkyl group. This is analogous behaviour to that reported when these radicals react with alkanes, i.e., $\Delta E \sim 3$ kcal $mole^{-1}$, $A_{CF_3} \sim A_{CH_3}$. For example, with ethane [13] as the substrate molecule, the Arrhenius parameters are (CF_3), log A = 11·7, E = 7·5, and (CH_3), log A = 11·1, E = 10·4 kcal $mole^{-1}$, and $k_{CF_3}/k_{CH_3} \sim 100$.

Hydrogen atom abstraction from the hydroxyl group shows marked differences between the two radicals, although again the polar radical is more reactive by a afctor of *ca.* 90. The activation energy requirements differ by 5·8 kcal $mole^{-1}$ and the A-factor for the reaction involving CF_3 radicals is appreciably lower than the values frequently observed for such abstraction reactions. We consider that this may be explained as follows: to abstract the hydroxylic hydrogen atom the polar CF_3 radical will be more restricted in its direction of approach for a collision leading to reaction than for abstraction of the hydrogen atom attached to the carbon atom. This is because of the strong repulsion forces which may be expected between the radical and the functional group of the methanol. Because of this effect there will

be a low steric factor, although if steric requirements are fulfilled there will be a high likelihood of reaction because of the low activation energy for reaction (12). Since attack on the alkyl group is not subject to such directional limitations a "normal" A-factor would be expected and is in fact observed. When methyl radicals react with methanol repulsion forces are not so marked and "normal" A-factors result.

ABSTRACTION OF HYDROGEN IN CF_3H BY CH_3O RADICALS

Rate constants and Arrhenius parameters for hydrogen atom abstractions reactions by methoxyl radicals from a variety of substrate molecules have been reported. By using data for reaction (12)

$$CF_3 + CH_3OH \underset{-12}{\overset{12}{\rightleftharpoons}} CF_3H + CH_3O$$

in conjunction with the equilibrium constant $K(= k_{12}/k_{-12})$ we obtain information regarding the reactivity of CH_3O radicals with fluoroform. Using the following entropy values S°_{298} (cal deg.$^{-1}$ mole^{-1}), $(CH_3O) = 55$,[14] $(CF_3) = 60{\cdot}7$,[15] $(CF_3H) = 62{\cdot}0$ [15] and $(CH_3OH) = 56{\cdot}5$,[16] we find that $\Delta S \sim 0$ cal deg.$^{-1}$ mole^{-1}, so that $A_{-12} = A_{+12}$. To evaluate E_{-12} we need to know ΔH since $\Delta H = E_{12} - E_{-12}$. Using the JANAF values [15] for the heats of formation of CF_3 and CF_3H (viz., $-120{\cdot}5$ and $-162{\cdot}6$ kcal mole^{-1} respectively) a value of about 94 kcal mole^{-1} may be calculated for $D(CF_3—H)$ which seems extremely low. Kerr [17] has suggested that Whittles' value [18] of 106 kcal mole^{-1} is a more likely value. Using this value we find that $\Delta H = -4$ kcal mole^{-1} and since $E_{12} = 3{\cdot}2$ kcal mole^{-1}, then E_{-12} is 7·2 kcal mole^{-1}. The rate constant for reaction (-12) may therefore be represented by the equation:

$$\log k_{-12}\ (\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = 9{\cdot}5 - 7200/2{\cdot}303RT.$$

The rate constant so calculated is probably not accurate to better than an order or magnitude, but it does give a guide to the reactivity of the methoxyl radical.

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REACTIONS OF RADICALS CONTAINING FLUORINE

PART 2.—HYDROGEN AND DEUTERIUM ATOM ABSTRACTION FROM METHYLAMINE AND TRIDEUTEROMETHYLAMINE BY TRIFLUOROMETHYL RADICALS

Reactions of Radicals Containing Fluorine

Part 2.—Hydrogen and Deuterium Atom Abstraction from Methylamine and Trideuteromethylamine by Trifluoromethyl Radicals.

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The reactions of trifluoromethyl radicals with methylamine and trideuteromethylamine have been studied in the temperature range 30-160°C in order to determine the rates at which hydrogen and deuterium atoms are abstracted from the molecules. With methylamine, radical attack is favoured at the alkyl position, and substitution of deuterium for hydrogen alters the positional reactivity by an amount in accord with the zero-point energy difference. The pre-exponential factors for attack at the nitrogen site have been explained in terms of a low steric factor due to repulsion forces between the polar molecule and the radical. Arrhenius parameters (based upon a value of $10^{13\cdot34}$ mole^{-1} cm^3 sec^{-1} for the rate constant of combination of trifluoromethyl radicals) have been measured for the reactions:

$CF_3+CD_3NH_2\rightarrow CF_3H+CD_3NH$	$9\cdot94\pm0\cdot22$	$4\cdot4\pm0\cdot4$
$CF_3+CD_3NH_2\rightarrow CF_3D+CD_2NH_2$	$11\cdot03\pm0\cdot09$	$6\cdot1\pm0\cdot2$
$CF_3+CH_3NH_2\rightarrow CF_3H+(CNH_4)$	$10\cdot79\pm0\cdot16$	$4\cdot2\pm0\cdot3$
$CF_3+CH_3NH_2\rightarrow CF_3H+CH_2NH_2$	$10\cdot72\pm0\cdot39$	$4\cdot2\pm0\cdot6$

and have been calculated for

$NHCH_3+CF_3H\rightarrow NH_2CH_3+CF_3$	9·9	18·4

(units of A, mole^{-1} cm^3 sec^{-1}; and E, kcal mole^{-1}).

The abstraction of hydrogen atoms from various hydrocarbons by trifluoromethyl radicals has been studied by several workers [1-3] and in general it appears that such reactions proceed faster and have lower activation energy requirements than do the corresponding reactions involving alkyl radicals. There have been few studies of hydrogen atom abstraction reactions by fluoroalkyl radicals with molecules where there are abstractable hydrogen atoms attached to two different atoms, e.g., with methyl mercaptan or with methylamine. Since data are available for the reaction of methyl radicals with methylamine-d_3 and methylamine [4] it was decided to compare the reactivities of methyl and trifluoromethyl radicals with these substrates using trideuteromethylamine to evaluate the separate contributions involving the C—H and N—H bonds. Our results also enable a kinetic isotope effect to be assessed for the methyl and trideuteromethyl groups.

EXPERIMENTAL

The photolysis of hexafluoroacetone is frequently used as a convenient source of trifluoromethyl radicals in hydrogen-atom abstraction studies. With substrates such as methylamine hexafluoroacetone reacts rapidly to form a rather involatile solid. Trifluoromethyl iodide (TFMI) does not react with these compounds and accordingly we have chosen the photolysis of TFMI as our radical course. TFMI has another advantage, that secondary reactions between trifluoromethyl radicals and the radical species R formed in the initial hydrogen atom abstraction

$$CF_3+RH\rightarrow CF_3H+R$$

are reduced or inhibited by the iodine present in the reacting system.

MATERIALS

TRIFLUOROMETHYL IODIDE was prepared by heating a 1 : 3 intimate mixture of silver trifluoroacetate (Koch-Light) and iodine in a closed system under slightly reduced pressure and collecting the gas evolved in a series of cold traps. Impurities such as fluoroform, hexafluoroethane and carbon dioxide were removed by extensive pumping at −130°C on a vacuum line.

TRIDEUTEROMETHYLAMINE was prepared from the hydrochloride salt (E. Merck A. G. Darmstadt) by dropping potassium hydroxide solution on the salt and collecting the gas evolved from the warmed solution. It was further purified by fractionating several times at −78°C before storage on the vacuum line.

METHYLAMINE was similarly prepared from the hydrochloride.

APPARATUS AND PROCEDURE

The essential details of the apparatus used and the analytical technique employed have been described.[5] Decomposition of the substrate was usually 1-2 %.

RESULTS AND DISCUSSION

CF_3H AND C_2F_6 FORMATION DURING PHOTOLYSIS OF TFMI IN THE PRESENCE OF TRIDEUTEROMETHYLAMINE

When trifluoromethyl radicals, generated by the photolysis of trifluoromethyl iodide, react with trideuteromethylamine, CF_3H, CF_3D and C_2F_6 are observed

TABLE 1.—HYDROGEN AND DEUTERIUM ATOM ABSTRACTION FROM TRIDEUTEROMETHYLAMINE BY TRIFLUOROMETHYL RADICALS.

T(°K)	t (sec)	CD_3NH_2	CF_3I	CF_3H	CF_3D	C_2F_6	$k_1/k_3^{\frac{1}{2}}$	$k_2/k_3^{\frac{1}{2}}$
302·9	250	1·15	1·74	9·82	5·53	29·2	1·59	0·89
303·2	150	1·19	1·25	9·44	6·49	24·0	1·61	1·10
312·5	450	0·61	0·68	4·39	3·84	20·5	1·59	1·40
322·6	250	0·99	1·04	7·52	7·13	14·3	2·01	1·90
333·3	450	0·73	0·75	5·32	6·95	13·3	2·00	2·61
344·9	150	0·66	1·00	10·3	10·8	20·9	3·43	3·59
357·1	750	0·68	0·94	3·46	5·26	3·66	2·65	4·02
357·1	450	0·61	0·68	4·62	6·18	6·77	2·91	3·90
370·3	600	0·81	0·85	6·13	8·86	3·57	4·01	5·81
370·4	150	0·72	1·09	12·2	15·3	10·1	5·34	6·73
384·6	600	0·65	0·89	4·42	7·21	2·44	4·33	7·06
400·0	500	0·57	0·59	7·86	13·0	4·03	6·85	11·3
416·6	150	0·96	1·01	19·2	25·9	2·89	11·7	15·8
434·8	450	0·53	0·60	14·9	22·5	3·71	14·4	21·9
434·8	450	0·60	0·82	14·1	23·5	2·95	13·7	22·7

CD_3NH_2 and CF_3I in 10^6 mole cm^{-3}.
CF_3H, CF_3D and C_2F_6 in 10^{12} mole cm^{-3} sec^{-1}.

as reaction products and they are accounted for by the following reaction scheme:

$$CF_3 + CD_3NH_2 \xrightarrow{1} CF_3H + CD_3NH$$

$$\xrightarrow{2} CF_3D + CD_2NH_2$$

$$2CF_3 \xrightarrow{3} C_2F_6,$$

and the following steady-state equations apply:

$$\frac{R_{CF_3H}}{R_{C_2F_6}^{\frac{1}{2}}[CD_3NH_2]} = \frac{k_1}{k_3^{\frac{1}{2}}} \quad \text{and} \quad \frac{R_{CF_3D}}{R_{C_2F_6}^{\frac{1}{2}}[CD_3NH_2]} = \frac{k_2}{k_3^{\frac{1}{2}}}$$

where $[CD_3NH_2]$ denotes the concentration of trideuteromethylamine and R_X the rate of formation of X.

Our results are shown in table 1. When treated by the method of least-mean-squares they are represented by the equations:

$$\log k_1 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (9{\cdot}94 \pm 0{\cdot}22) - (4390 \pm 370)/2{\cdot}303\, \boldsymbol{RT}.$$

and

$$\log k_2 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (11{\cdot}03 \pm 0{\cdot}09) - (6050 \pm 160)/2{\cdot}303\boldsymbol{RT}.$$

The error limits quoted represent the standard deviations of a least-mean-squares computer treatment.

We have used the value of $10^{13{\cdot}34}$ mole^{-1} cm^3 sec^{-1} obtained by Ayscough [6] for the rate constant k_3 for the combination of trifluoromethyl radicals. There are no Arrhenius parameters reported for the above reactions with which our values may be compared.

IN THE PRESENCE OF METHYLAMINE

When trifluoromethyl iodide is photolyzed in the presence of unlabelled methylamine, the fluoroform formation indicates only the total attack of trifluoromethyl radicals on the substrate, i.e., reaction (4) represents the sum of the individual reactions (5) and (6). Hence k_4 is not a meaningful velocity constant, being a composite value of k_5 and k_6:

$$CF_3 + CH_3NH_2 \xrightarrow{4} CF_3H + (CNH_4)$$
$$\xrightarrow{5} CF_3H + CH_3NH$$
$$\xrightarrow{6} CF_3H + CH_2NH_2.$$

Our data are reported in table 2 and for the overall velocity constant k_4 are represented by

$$\log k_4 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (10{\cdot}79 \pm 0{\cdot}16) - (4190 \pm 260)/2{\cdot}303\, \boldsymbol{RT}.$$

Secondary isotope effects are usually insignificant [7-9] in reactions such as those quoted above. If the secondary isotope effect is zero [4] then the difference in the velocity constants for CF_3H formation from CH_3NH_2 and CD_3NH_2 equals the velocity constant k_6 for CF_3H formation by attack on the methyl group in CH_3NH_2.

With the assumption that $k_1 = k_5$, we find that

$$\log k_6 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (10{\cdot}72 \pm 0{\cdot}39) - (4170 \pm 650)/2{\cdot}303\, \boldsymbol{RT}.$$

Evaluation of the velocity constants k_3 and k_6 enable a quantitative comparison of the reactivity of the hydrogen atoms in the amino and methyl groups of methylamine to be made. The methyl group is more reactive towards radical attack, at 164°C (where 2·303 $\boldsymbol{RT}$ is 2000) k_4 and k_6 having values of $10^{7{\cdot}7}$ and $10^{8{\cdot}6}$ mole^{-1} cm^3 sec^{-1} respectively. Hence at this temperature for every eight hydrogen atoms abstracted seven come from the methyl group. This is in sharp contrast with the results reported for methyl radical attack on methylamine which indicate (see table 3) that the methyl and amino groups have similar reactivities (on an overall basis) at 164°C. In terms of the number of hydrogen atoms available for reaction, the amino group is slightly the more reactive. For methanol the methyl group is less reactive than the hydroxyl

group (on a per-atom basis) towards attack by both methyl and trifluoromethyl and again the difference is most apparent with the polar radical.

Pritchard *et al.*[2] have shown that, for many hydrocarbons, the activation energies required for hydrogen atom abstraction by trifluoromethyl radicals are ~3-4 kcal

TABLE 2.—HYDROGEN ATOM ABSTRACTION FORM METHYLAMINE BY TRIFLUOROMETHYL RADICALS

T(°K)	t (sec)	CH_3NH_2	CF_3I	CF_3H	C_2F	$k_4/k_3^{\frac{1}{2}}$
302·9	100	1·21	1·22	90·1	57·5	9·8
303·1	200	0·625	1·86	48·9	69·3	9·4
312·4	50	0·518	1·54	78·3	70·7	18·0
322·6	100	1·12	1·13	128·0	48·9	16·3
333·3	50	0·903	0·797	50·0	4·64	25·7
333·3	50	0·657	1·95	115·1	66·8	21·5
333·3	50	0·193	1·97	40·4	45·5	31·0
333·3	500	0·159	1·95	8·47	3·37	29·3
333·3	500	1·010	0·892	33·8	1·86	24·8
333·3	600	1·483	0·559	32·1	0·637	27·3
344·6	150	0·845	0·849	111·6	26·8	25·5
357·1	150	0·186	1·90	26·5	18·0	33·5
370·3	150	0·478	1·42	73·8	16·6	37·9
384·6	50	0·174	1·78	44·0	19·4	57·4
399·8	100	0·933	0·938	184·7	8·68	67·2
416·3	180	0·388	1·50	79·7	9·66	66·1
416·3	100	0·348	1·46	93·0	13·1	73·7
434·8	150	0·147	1·50	48·1	9·08	108·7

CH_3NH_2 and CF_3I in 10^6 mole cm^{-3}.
CF_3H and C_2F_6 in 10^{12} mole cm^{-3} sec^{-1}.

TABLE 3.—COMPARISON OF VELOCITY CONSTANTS AT 164°C AND ARRHENIUS PARAMETERS FOR ABSTRACTION REACTIONS BY CH_3 AND CF_3 RADICALS

reaction	log A (mole^{-1} cm^3 sec^{-1})	E (kcal mole^{-1})	log k (164°C) overall	per H-atom	ref.
$CF_3+CH_4\rightarrow CF_3H+CH_3$	11·7	10·3	6·6	6·0	17
$CH_3+CH_4\rightarrow CH_4+CH_3$	11·8	14·7	4·5	3·9	18
$CF_3+\underline{CD_3}NH_3\rightarrow CF_3D+CD_2NH_2$	11·03	6·1	8·0	7·5	this work
$CF_3+\underline{CD_3}NH_2\rightarrow CF_3H+CD_3NH$	9·94	4·4	7·7	7·4	this work
$CF_3+\underline{CH_3}NH_2\rightarrow CF_3H+CH_2NH_2$	10·73	4·2	8·6	8·1	this work
$CH_3+\underline{CH_3}NH_2\rightarrow CH_4+CH_3NH$	9·55	5·7	6·7	6·4	4
$CH_3+\underline{CH_3}NH_2\rightarrow CH_4+CH_2NH_2$	10·99	8·7	6·6	6·1	4
$CF_3+\underline{CD_3}OH\rightarrow CF_3H+CD_3O$	9·5	3·2	7·9	7·9	5
$CF_3+\underline{CH_3}OH\rightarrow CF_3H+CH_2OH$	10·0	4·7	7·7	7·2	5
$CH_3+\underline{CD_3}OH\rightarrow CH_4+CD_3O$	10·46	9·0	6·0	6·0	10
$CH_3+\underline{CH_3}OH\rightarrow CH_4+CH_2OH$	10·38	8·1	6·3	5·8	10
$CF_3+\underline{CH_3}CH_3\rightarrow CF_3H+C_2H_5$	11·7	7·5	7·9	7·1	17
$CH_3+\underline{CH_3}CD_3\rightarrow CH_4+C_2H_2D_3$	11·9	11·8	6·0	5·5	7

The hydrogen atom which is abstracted is underlined for methylamine, methanol and ethane-d_3.

mole^{-1} lower and the reaction rates much higher than for the corresponding reactions involving methyl radicals. Comparison of the Arrhenius parameters determined for reaction (6) with the values established [4] for the reaction

$$CH_3+CH_3NH_2\rightarrow CH_4+CH_2NH_2$$

shows that the pre-exponential factors are similar (10·73 and 10·99 respectively) but there is an activation energy difference of about 4·5 kcal mole^{-1}, so that the alkyl group in a polar molecule behaves in a similar manner as in a hydrocarbon, ie., there is a lowering of the activation energy required for abstraction by the CF_3 radical.

Of particular interest is the pre-exponential factor for reaction (1) which is lower than the values frequently reported for hydrogen atom abstraction reactions, particularly with hydrocarbon substrates. Benson and DeMore [11] have suggested that such values are the result of the occurrence of secondary reactions between the primary radical and the product radical. We consider this not to be the explanation for such values partly because of the small extent of reaction (1-2 %) and because variation of the [TFMI]/[CH_3NH_2] ratio over a thirty-fold range showed no variation in the rate constant ratio outside that attributable to the experimental error involved in measuring small quantities of C_2F_6. Also, variation in the reaction times by a factor of ten showed no alteration in the rate constant ratio. In addition, a study [5] of the reaction of trifluoromethyl radicals with n-butane has indicated that the occurrence of facile secondary reactions does not give rise to such low pre-exponential factors. Unpublished results obtained in this laboratory have indicated similar behaviour with cyclohexane.

An investigation of the reaction of trifluoromethyl radicals with methanol [5] has shown that a similar situation exists for this molecule, i.e., a " normal " pre-exponential factor for attack on the methyl group and a " low value " ($10^{9\cdot5}$) for the hydroxyl group. We consider that the results for methanol and methylamine may be interpreted in terms of the strong repulsion forces which are likely between the polar radical and the function group of the substrate molecule. Because of this, the polar radical will be restricted in its approach to the molecule for a reactive collision involving the functional group, and as a consequence there will be a low steric factor for such a reaction. If steric conditions are satisfied there will be a high likelihood of reaction because the activation energy requirements are small. Attack on the methyl group of the polar molecule is not so subject to steric limitations and hence " normal " pre-exponential factors are to be expected and are observed.

PRIMARY ISOTOPE EFFECTS IN CF_3 RADICAL ATTACK ON METHYLAMINE

The results reported above enable a primary kinetic isotope effect to be deduced for the methyl and trideuteromethyl groups in methylamine. Comparison of the velocity constants k_2 and k_6 shows that a hydrogen atom is abstracted more readily than is a deuterium atom, the ratio k_6/k_2 varying with temperature with a value of 4·1 at 164°C.

Below we have compared our data for the primary isotope effect with results reported for several similar substrates for methyl and trifluoromethyl radicals. In all cases the ratio A_H/A_D is near to the expected value of unity, though the fact that in the examples the ratio is slightly less than one may not be significant since the deviation is within the experimental error in all cases. Activation energy differences,

radical	substrates	A_H/A_D	E_D-E_H (kcal mole^{-1})	k_H/k_D(164°)	z.p.e. (kcal mole^{-1})	ref.
CF_3	CD_3NH_2,CH_3NH_2	0·5	1·8	4·1	1·2	this work
CF_3	CD_3OH,CH_3OH	0·6	1·9	5·6	1·2	5
CH_3	CD_3NH_2,CH_3NH_2	0·9	1·3	6·4	1·2	4
CH_3	CH_3ND_2,CH_3NH_2	0·8	1·3	4·4	1·3	4
CH_3	CD_3OH,CH_3OH	0·6	1·1	6·3	1·2	10

$E_D - E_H$, are close to the zero-point energy difference (z.p.e.) of 1·2 kcal mole^{-1} corresponding to a single C—H and C—D stretching vibration.

REACTIONS OF $NHCH_3$ RADICALS

There are few kinetic data available for nitrogen containing radicals, particularly regarding their ability to abstract hydrogen atoms from substrate molecules. This is partly due to the experimental difficulties inherent in direct studies of such reactions. It is possible, however, to determine such data indirectly from a study of the reverse reaction in conjunction with a knowledge of the thermodynamics of the overall reaction since the Arrhenius parameters of the forward and back reactions are related [12] by the expressions:

$$\log (A_f/A_b) = \Delta S^\circ/2{\cdot}303R, \text{ and } E_f - E_b = \Delta H^\circ.$$

By using the data reported above for reaction (1) we can evaluate the Arrhenius parameters for reaction (7),

$$NHCH_3 + CF_3H \xrightarrow{7} NH_2CH_3 + CF_3,$$

where the methylamino radicals abstract hydrogen from fluoroform.

Using the following entropy values, S°_{298} (cal deg.$^{-1}$ mole^{-1}), $(NHCH_3) = 56{\cdot}4$,[3] $(NH_2CH_3) = 57{\cdot}7$,[13] $(CF_3) = 60{\cdot}7$ [14] and $(CF_3H) = 62{\cdot}0$,[14] we find that for reaction (7) the overall entropy change ΔS° is close to zero, i.e., $A_1 = A_7$.

The enthalpy change ΔH° is related to the difference between the strengths of the bonds formed and broken and hence depends on $D(CF_3-H)$. Although no direct determination has been made it seems well established [15] that Whittle's value [16] of 106 kcal mole^{-1} is likely to be accurate. Using this value together with the value [19] of 92 kcal mole^{-1} reported for $D(CH_3NH-H)$, we find that the velocity constant for reaction (7) is represented by the equation:

$$\log k_7 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 9{\cdot}9 - 18400/2{\cdot}303\,RT.$$

The rate constant calculated in this manner is probably not accurate to better than an order of magnitude but the equation gives a guide to the relative reactivities of the radical.

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REACTIONS OF RADICALS CONTAINING FLUORINE

PART 3.—HYDROGEN AND DEUTERIUM ATOM ABSTRACTION FROM DIMETHYLAMINE, DIMETHYLAMINE-D, TRIMETHYLAMINE AND ETHYLENEIMINE

Reactions of Radicals containing Fluorine

Part 3.—Hydrogen and Deuterium Atom Abstraction from Dimethylamine, Dimethylamine-d, Trimethylamine and Ethyleneimine

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The reactions of trifluoromethyl radicals with dimethylamine, dimethylamine-d, trimethylamine and ethyleneimine have been studied in the temperature range 27-161°C. Arrhenius parameters (based upon a value of $10^{13\cdot37}$ mole^{-1} cm^3 sec^{-1} for the velocity constant for the combination of trifluoromethyl radicals) have been obtained for the reactions:

	$\log_{10} A$(mole^{-1} cm^3 sec^{-1})	E(kcal mole^{-1})
$CF_3+(CH_3)_2NH \rightarrow CF_3H+C_2H_6N$	11·45±0·12	4·1±0·2
$CF_3+(CH_3)_2ND \rightarrow CF_3D+(CH_3)_2N$	10·88±0·29	4·7±0·5
$CF_3+(CH_3)_2NH \rightarrow CF_3H+(CH_3)_2N$	10·5±0·7	3·3±1·0
$CF_3+(CH_3)_2ND \rightarrow CF_3H+CH_3(CH_2)ND$	11·82±0·51	5·1±0·8
$CF_3+(CH_3)_3N \rightarrow CF_3H+(CH_3)_2NCH_2$	11·82±0·12	4·5±0·2
$CF_3+(CH_2)_2NH \rightarrow CF_3H+C_2H_4N$	11·00±0·17	4·1±0·3

With dimethylamine, radical attack is favoured, on a " per-atom basis," at the nitrogen atom but the difference in reactivities of the C—H and N—H bonds is much less marked than with methyl radicals. Assuming a zero secondary isotope effect, substitution of D for H in dimethylamine alters the reactivity of the amino group by an amount in accord with zero-point-energy difference.

The reactions of methyl radicals with a wide variety of nitrogen-containing compounds have been studied [1-5] and information obtained regarding the positions and rates of hydrogen atom abstraction from the substrates. Trifluoromethyl radicals also readily abstract hydrogen from such molecules and their reactions with trideuteromethylamine and methylamine have been examined.[6] We have extended this investigation to dimethylamine, trimethylamine and ethyleneimine.

EXPERIMENTAL

The apparatus used and experimental technique employed have been described.[7]

MATERIALS. Dimethylamine, trimethylamine and ethyleneimine were commercial samples which were purified by low-temperature distillation on the vacuum line.

Dimethylamine-d was prepared by shaking dimethylamine with acidified D_2O at 25°C for 24 h followed by low-temperature distillation. This procedure was repeated and the extent of deuteration was followed by measuring the 730 cm^{-1} band in the infra-red spectrum which shifts to 587 cm^{-1} on deuteration. The sample was dried by low-temperature bulb-to-bulb distillation before being stored on the vacuum line. The sample used contained 63 % dimethylamine-d_1.

RESULTS

Hexafluoroacetone is frequently used as a photochemical source of trifluoromethyl radicals; however, it reacts to form a white involatile solid with amines. We have chosen the photolysis of trifluoromethyl iodide (TFMI) as the source of free radicals since no reaction (as evidenced by there being no pressure change) occurred when this was mixed with any of the compounds used in this investigation.

PHOTOLYSIS OF TFMI IN THE PRESENCE OF TRIMETHYLAMINE

When TFMI is photolyzed in the presence of trimethylamine the reaction products observed and analyzed for were CF_3H and C_2F_6. Their formation and distribution are accounted for by reactions (1) and (2):

$$CF_3 + (CH_3)_3N \xrightarrow{1} CF_3H + (CH_3)_2NCH_2$$

$$2\,CF_3 \xrightarrow{2} C_2F_6.$$

The following relationship may be derived:

$$R_{CF_3H}/R^{\frac{1}{2}}_{C_2F_6}[(CH_3)_3N] = k_1/k_2^{\frac{1}{2}},$$

where R_X refers to the rate of formation of X and $[(CH_3)_3N]$ is the mean concentration of trimethylamine. Our experimental data are shown in table 1.

If a value of $10^{13\cdot37}$ (mole^{-1} cm^3 sec^{-1}) is used for the rate constant for the combination of trifluoromethyl radicals,[8] our results are expressed by the equation:

$$\log k_1(\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = 11{\cdot}85 \pm 0{\cdot}12 - (4460 \pm 190)/2{\cdot}303\ \boldsymbol{RT},$$

where the error limits represent the standard deviation of a least-mean-squares computer treatment. The uncertainty in $k_2(\sim 10^{\pm 0\cdot 2})$ has not been included in the error limits quoted in this paper.

TABLE 1.—HYDROGEN ATOM ABSTRACTION FROM TRIMETHYLAMINE BY TRIFLUOROMETHYL RADICALS

T(°K)	t(sec)	$[(CH_3)_3N]$	$[CF_3I]$	$[CF_3H]$	$[C_2F_6]$	$k_1/k_2^{\frac{1}{2}}$
303·0	100	0·175	1·761	67·1	18·8	88·6
303·3	45	1·008	1·003	390·2	21·6	83·3
322·5	100	0·164	1·651	93·9	14·6	150
344·8	100	0·174	1·759	150·4	14·0	230
370·3	45	1·117	1·110	1008	10·6	277
400·0	120	0·221	1·192	350·8	12·5	448
400·0	45	0·305	1·248	720·5	17·3	568
434·8	30	0·387	1·586	1215	12·7	879
434·8	60	0·266	1·091	683·5	9·95	813

$(CH_3)_3N$ and CF_3I in 10^6 mole cm^{-3}; CF_3H and C_2F_6 in 10^{12} mole cm^{-3} sec^{-1}; $k_1/k_2^{\frac{1}{2}}$ in mole$^{-\frac{1}{2}}$ cm$^{\frac{3}{2}}$ sec$^{-\frac{1}{2}}$.

PHOTOLYSIS OF TFMI IN THE PRESENCE OF ETHYLENEIMINE

Since in ethyleneimine hydrogen atoms are attached to the carbon and also to the nitrogen atoms, it is probable that CF_3H formation can occur by trifluoromethyl radical attack at both sites, i.e., reaction (3) represents the sum of the contributions from reactions (4) and (5).

$$CF_3 + (CH_2)_2NH \xrightarrow{3} CF_3H + C_2NH_4$$

$$\xrightarrow{4} CF_3H + CH_2(CH)NH$$

$$\xrightarrow{5} CF_3H + (CH_2)_2N.$$

Gray and Jones have [4] studied the reaction of methyl radicals with ethyleneimine and, using a deuterium-labelling technique, have concluded that at 150°C the hydrogen

atom attached to the nitrogen atom is about 160 times more reactive than the corresponding hydrogen atom linked to the carbon atom. We have assumed that a similar situation exists for trifluoromethyl radicals and that data obtained for the overall-reaction represents closely the abstraction from the N—H bond, i.e., that $k_3 = k_5$.

Our experimental data are recorded in table 2 and are represented by the expression:

$$\log k_3(\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = 11{\cdot}03 \pm 0{\cdot}17 - (4140 \pm 270)/2{\cdot}303\ \boldsymbol{RT}.$$

TABLE 2.—HYDROGEN ATOM ABSTRACTION FROM ETHYLENEIMINE BY TRIFLUOROMETHYL RADICALS

T(°K)	t(sec)	$[(CH_2)_2NH]$	$[CF_3I]$	$[CF_3H]$	$[C_2F_6]$	$k_3/k_2^{\frac{1}{2}}$
303·1	45	0·429	1·758	57·3	40·6	20·9
322·5	45	1·951	0·771	110·2	3·94	28·5
344·8	45	0·252	1·003	59·7	21·1	51·4
370·3	45	0·384	1·575	135·7	26·9	68·0
400·0	90	1·536	0·607	206·1	2·42	86·3
434·8	45	0·387	1·588	470·0	55·2	163
434·8	90	0·540	1·032	296·5	9·19	180

$(CH_2)_2NH$ and CF_3I in 10^6 mole cm^{-3}; CF_3H and C_2F_6 in 10^{12} mole cm^{-3} sec^{-1}; $k_3/k_2^{\frac{1}{2}}$ in mole$^{-\frac{1}{2}}$ cm$^{\frac{3}{2}}$ sec$^{-\frac{1}{2}}$.

PHOTOLYSIS OF TFMI IN THE PRESENCE OF DIMETHYLAMINE

$$CF_3 + (CH_3)_2NH \xrightarrow{6} CF_3H + C_2H_6N$$
$$\xrightarrow{7} CF_3H + CH_3(CH_2)NH$$
$$\xrightarrow{8} CF_3H + (CH_3)_2N$$

Hydrogen atom abstraction occur from both the C—H and N—H bonds, so that reaction (6) represents the overall sum of the contributions of reactions (7) and (8). Our results for the overall abstraction are given in table 3 and are expressed by

$$\log k_6(\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = 11.48 \pm 0{\cdot}12 - (4140 \pm 180)/2{\cdot}303\ \boldsymbol{RT}.$$

A study of the reaction of methyl radicals with dimethylamine [3] has shown that, unlike for ethyleneimine, there is not such a large difference between the reactivity of the hydrogen atoms attached to the carbon and nitrogen atoms. Consequently, the individual contributions of reactions (7) and (8) may only be assessed by suitable labelling of dimethylamine.

We have investigated the reaction of CF_3 radicals with dimethylamine-d_1 containing 37 % $(CH_3)_2NH$, and measured the CF_3H and CF_3D produced by reactions (9) and (10):

$$CF_3 + (CH_3)_2ND \xrightarrow{9} CF_3D + (CH_3)_2N$$
$$\xrightarrow{10} CF_3H + CH_3(CH_2)ND.$$

A correction was made for the CF_3H formed by reaction with the unlabelled amine (reaction (6)) before a comparison may be made between reactions (9) and (10).

This correction, together with the facts that the yield of CF_3D is generally much less than that of CF_3H and that relatively small amounts of C_2F_6 are formed, results in our data being subject to a large experimental error. Our data are shown in table 4 and, after least-squares analysis, are expressed by the equations:

$$\log k_9(\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = 10{\cdot}91 \pm 0{\cdot}29 - (4710 \pm 460)/2{\cdot}303\ \boldsymbol{RT},$$

and

$$\log k_{10}(\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = 11{\cdot}85 \pm 0{\cdot}51 - (5060 \pm 820)/2{\cdot}303\ \boldsymbol{RT}.$$

TABLE 3.—HYDROGEN ATOM ABSTRACTION FROM DIMETHYLAMINE BY TRIFLUOROMETHYL RADICALS

T(°K)	t(sec)	$[(CH_3)_2NH]$	$[CF_3I]$	$[CF_3H]$	$[C_2F_6]$	$k_6/k_2^{\frac{1}{2}}$
370·3	90	0·295	0·767	228	14·5	211
370·3	45	0·554	0·794	357	8·53	224
357·1	90	0·694	0·690	44·1	0·14	170
344·8	300	0·183	1·83	25·8	0·84	156
344·8	900	0·187	1·87	28·6	1·28	145
333·3	150	1·25	1·26	193	2·12	107
333·3	45	0·481	1·25	328	40·6	108
333·3	45	0·902	1·29	490	27·1	106
322·6	1100	0·124	1·24	11·5	1·02	96·5
322·6	90	0·479	1·36	30·3	0·52	88·6
322·6	900	0·476	1·35	31·7	0·45	102
312·7	90	0·591	1·54	307	54·2	72·2
303·0	300	0·345	1·66	18·8	0·75	63·5
303·0	1500	0·359	1·73	13·8	0·39	63·5

$(CH_3)_2NH$ and CF_3I in 10^6 mole cm^{-3}; CF_3H and C_2F_6 in 10^{12} mole cm^{-3} sec^{-1}; $k_6/k_2^{\frac{1}{2}}$ in $mole^{-\frac{1}{2}}$ $cm^{\frac{3}{2}}$ $sec^{-\frac{1}{2}}$.

TABLE 4.—HYDROGEN AND DEUTERIUM ATOM ABSTRACTION FROM DIMETHYLAMINE-d_1 BY TRIFLUOROMETHYL RADICALS

T(°K)	t(sec)	$[(CH_3)_2ND]$	$[CF_3I]$	$[CF_3H]$	$[CF_3D]$	$[C_2F_6]$	$k_{10}/k_2^{\frac{1}{2}}$	$k_9/k_2^{\frac{1}{2}}$
370·3	90	0·496	1·003	226	40·8	8·64	155	28·0
370·3	300	0·330	1·009	613	11·2	2·08	129	23·6
370·3	300	0·234	0·817	57	9·1	1·96	174	27·7
370·3	45	0·463	1·115	197	37·5	7·54	155	29·5
357·1	90	0·511	0·765	95	20·7	5·21	81·1	17·8
344·8	90	0·908	0·641	94	18·0	1·59	82·0	15·7
333·3	90	0·338	0·814	75	13·2	7·01	83·1	14·7
333·3	90	0·791	1·181	85	18·4	3·66	56·2	12·2
322·6	90	1·438	1·013	125	23·3	2·54	54·8	10·2

$(CH_3)_2ND$ and TFMI in 10^6 mole cm^{-3}; CF_3H, CF_3D and C_2F_6 in 10^{12} mole cm^{-3} sec^{-1}; $k_4/k_2^{\frac{1}{2}}$ and $k_{10}/k_2^{\frac{1}{2}}$ in $mole^{-\frac{1}{2}}$ $cm^{\frac{3}{2}}$ $sec^{-\frac{1}{2}}$.

We can derive Arrhenius parameters for reaction (8) using our results for reactions (6) and (10) if we assume that secondary isotope effects [1, 9] are insignificant, i.e., $k_7 = k_{10}$. Our data indicate that the velocity constant, k_8, is expressed by

$$\log k_8(\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = 10{\cdot}5 \pm 0{\cdot}7 - (3300 \pm 1000)/2{\cdot}303\ \boldsymbol{RT}.$$

DISCUSSION

PRIMARY ISOTOPE EFFECT

Our results enable a primary isotope effect to be deduced for trifluoromethyl radical attack on the N—H and N—D bonds in dimethylamine and dimethylamine-d. Comparison of k_8 and k_9 indicates that hydrogen atom abstraction occurs more readily than that of a deuterium atom, the velocity constant ratio k_H/k_D having a value of approximately 3 at 77°C. Comparison of the Arrhenius parameters for reactions (8) and (9) indicate that, within the appreciable experimental error, the pre-exponential factors are similar. The difference in reactivity of the N—H and N—D arises mainly because of the difference in the activation energy requirements. This difference, although subject to a large experimental error, is comparable with the zero-point energy difference ΔE_0 of 1·3 kcal mole^{-1}, corresponding to a single N—H and N—D vibration. This observation is in accord with the primary isotope effects reported for several other systems involving methyl or trifluoromethyl radicals.[1, 2, 6]

COMPARISON OF REACTIVITY OF METHYL AND AMINO GROUPS IN DIMETHYLAMINE

Knowledge of the velocity constants for reactions (10) and (8) enable a quantitative comparison of the ease of hydrogen atom abstraction from the methyl and amino groups in dimethylamine. Attack on the N—H bond, which is weaker than the C—H bond, requires the lower activation energy by ~1·7 kcal mole^{-1}. The pre-exponential factors differ by about an order of magnitude being "normal" for abstraction from the alkyl group but lower for the amino group. Similar behaviour has been reported for methanol [7] and methylamine [6] and was interpreted in terms of the repulsion forces likely between the polar radical and the functional group of the molecule, thereby restricting the radical in its approach to the molecule for a reactive collision.

At 164°C the ratio of velocity constants k_{10}/k_8 is ~3 so that the methyl group is more reactive on an overall basis than is the amino group. On a per-hydrogen-atom-available basis, however, the hydrogen attached to the nitrogen is about twice as reactive as the hydrogen linked to the carbon atom. When methyl radicals are the abstracting species [3] the ratio of velocity constants is about 18, the N—H bond being the more reactive. The trifluoromethyl radical is markedly less selective in abstracting hydrogen than is the methyl radical and this is in keeping with the greater reactivity of the trifluoromethyl radical.

REACTIVITY OF N—H BONDS IN CH_3NH_2, $(CH_3)_2NH$ AND $(CH_2)_2NH$

In table 5 we have compared kinetic data for the abstraction of hydrogen from various substrates by methyl and trifluoromethyl radicals. In general, a similar pattern of reactivity is noted for both radicals, there being an increase in reactivity with decreasing bond strength, and activation energy requirements are *ca.* 1·5 kcal mole^{-1} lower for the trifluoromethyl radical attack on the N—H bonds. With methylamine and dimethylamine, the introduction of a second methyl group has the effect of markedly increasing the reactivity of the N—H bond towards attack by both CH_3 and CF_3 radicals.

REACTIVITY OF C—H BONDS IN CH_3NH_2, $(CH_3)_2NH$ AND $(CH_3)_3N$

The velocity constants for the abstraction of hydrogen attached to carbon increases as more hydrogen atoms are available in the molecule. For the series methylamine,

dimethylamine and trimethylamine, the velocity constants are in the ratio 1 : 4·5 : 10 for CF_3 attack and 1 : 3 : 6 for CH_3 attack. On a per-atom available basis the ratios are 1 : 2 : 3·5 and 1 : 1·5 : 2 respectively so that it appears that the $-NH_2$, >NH and >N groups do not have any marked difference in the activation of the C—H

TABLE 5.—HYDROGEN ATOM ABSTRACTION BY TRIFLUOROMETHYL AND METHYL RADICALS FROM AMINES AND RELATED COMPOUNDS

reaction	log A ($mole^{-1}$ cm^3 sec^{-1})	E (kcal $mole^{-1}$)	log k(164°) overall	log k(164°) per H-atom	ref.
$CF_3+\underline{CH_3}NH_2\rightarrow CF_3H$	10·7	4·2	8·6	8·1	6
$CH_3\underline{NH_2}\rightarrow CF_3H$	9·9	4·4	7·7	7·4	6
$CH_3+\underline{CH_3}NH_2\rightarrow CH_4$	11·0	8·7	6·7	6·2	1
$CH_3\underline{NH_2}\rightarrow CH_4$	9·55	5·7	6·7	6·4	1
$CF_3+(\underline{CH_3})_2NH\rightarrow CF_3H$	11·8	5·1	9·3	8·5	this work
$(CH_3)\underline{NH_2}\rightarrow CF_3H$	10·5	3·3	8·9	8·9	this work
$CH_3+(\underline{CH_3})_2NH\rightarrow CH_4$	11·5	8·7	7·2	6·4	3
$(CH_3)\underline{NH_2}\rightarrow CH_4$	10·8	6·4	7·6	7·6	3
$CF_3+(CH_3)_3N\rightarrow CF_3H$	11·8	4·5	9·6	8·7	this work
$CH_3+(CH_3)_3N\rightarrow CH_4$	11·8	8·8	7·4	6·5	11
$CF_3+(CH_2)_2NH\rightarrow CF_3H$	11·0	4·1	8·9	8·9	this work
$CH_3+(CH_2)_2NH\rightarrow CH_4$	10·3	4·8	7·9	7·9	4

The hydrogen atom which is abstracted is underlined.

bonds. Within experimental error there is little difference in the activation energies; the activation energies for abstraction from C—H bonds are about 4 kcal $mole^{-1}$ lower for trifluoromethyl radicals than for methyl radicals. Pritchard *et al.*[10] have reported that for abstraction from hydrocarbons there is an activation energy difference of about 3 kcal $mole^{-1}$.

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The Thermal Decomposition of Dimethyl Azodiformate

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The thermal decomposition in the gas and liquid phases of compounds of the type RN=NR to yield nitrogen and the free radical R is well known, data having been reported for systems where R is an alkyl,[1] alkoxyl,[2] or alkylamino[3] substituent.

$$RN{=}NR \longrightarrow N_2 + 2R\cdot \qquad (1)$$

The decompositions of formates[4-6] and carbonates[7] have demonstrated the instability of alkoxycarbonyl radicals, ĊOOR, which appear to decarboxylate quantitatively to generate an alkyl radical and carbon dioxide, and advantage has been taken of this reaction to generate free radicals not readily obtained by other methods

$$\dot{C}OOR \longrightarrow CO_2 + R\cdot \qquad (2)$$

A class of compounds which combines both of the above features is the esters of azodiformic acid, ROOCN=NCOOR. These compounds are easily prepared, are reddish, and decompose at temperatures above about 120°. They may be useful as potential thermal and photochemical sources of alkyl radicals, since by analogy with reactions 1 and 2 the following sequence of reactions might be expected

$$ROOCN{=}NCOOR \longrightarrow N_2 + 2\dot{C}OOR \qquad (3)$$

$$\dot{C}OOR \longrightarrow CO_2 + R\cdot \qquad (4)$$

Although the use of these compounds in connection with the Diels–Alder reaction is well known, their decomposition appears not to have been examined. We have studied the thermal decomposition of dimethyl azodiformate in the gas phase and in dodecane solution.

Experimental Section

Materials. Dimethyl azodiformate was prepared by the method of Rodgman and Wright,[8] a fraction boiling at 80.5° at 6.5 mm being collected. This was subjected to several bulb-to-bulb distillations on a vacuum line before being stored in a blackened bulb. Gas chromatographic analysis showed the sample to be pure.

Apparatus. In the gas-phase study, the azodiformate was condensed into a cylindrical Pyrex reaction vessel (volume 180 cm³) equipped with a break-seal and sealed off under vacuum. The reaction vessel was then immersed in a thermostated oil bath capable of maintaining temperatures up to 200° to better than ±1°. The reaction was stopped by removing the vessel from the oil bath and plunging it into a bath at −80°.

The reaction vessel was then sealed onto a high-vacuum line and the break-seal was broken. The reaction products were expanded into an analytical train which was comprised of a liquid nitrogen trap, a gas buret, and a Macleod gauge. The products not condensable in liquid nitrogen were collected and measured in the gas buret before being analyzed mass spectrometrically. A second fraction was removed at −121° using a pentane–liquid nitrogen slush bath and was similarly analyzed.

In the liquid-phase study, the decomposition was investigated in dodecane with 10^{-2} *M* solutions being used. The reaction vessels were cylindrical Pyrex tubes (volume *ca.* 5 cm³) which could be filled with solution leaving only a small space above the liquid. The ampoules were sealed off and the runs and analysis were performed as described above.

A similar analytical procedure was used for the photolysis studies, the light source being the full beam of a Mazda ME/D250W medium-pressure mercury lamp.

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Results and Discussion

Gas-Phase Decomposition. A series of runs were carried out at 162°. The noncondensable fraction contained no methane and consisted entirely of nitrogen. Analysis of the fraction volatile at −121° showed it to contain only about 3% ethane, the remainder being carbon dioxide with traces of the azodiformate ester. A typical product analysis yielded the following values (in micromoles): N_2, 205; CO_2, 1.94; and C_2H_6, 0.06; *i.e.*, $N_2/CO_2 = 1.06$ and $2C_2H_6/CO_2 = 0.06$.

$$CH_3OOCN{=}NCOOCH_3 \longrightarrow N_2 + 2CH_3OO\dot{C} \quad (5)$$

$$CH_3OO\dot{C} \longrightarrow CH_3 + CO_2 \quad (6)$$

Decomposition of the ester according to reactions 5 and 6 would require that the ratios N_2/CO_2 and $\Sigma CH_3\cdot/CO_2$ would have the values 0.5 and 1, respectively. We interpret the divergence of our experimental values from these predicted values to indicate that only about half of the methoxycarbonyl radicals generated in reaction 5 decompose. It appears that approximately 6% of the methyl radicals produced in the decarboxylation reaction are accounted for by the reaction

$$2CH_3\cdot \longrightarrow C_2H_6 \quad (7)$$

Methyl radicals have been shown to react very readily with azomethane[9] by addition to form trimethylhydrazine and tetramethylhydrazine. Our experimental results suggest that they may also react very readily with the azodiformate. It is likely also that some of the unaccounted for methoxycarbonyl radicals have reacted by addition to the N=N bond. Conjugation with the two carbonyl groups appears to have the effect of enhancing the rate of radical addition to the double bond. This reaction must be fast, since it is clearly competitive with reaction 6 and very much faster than the hydrogen atom abstraction reaction

$$CH_3\cdot + CH_3OOCN{=}NCOOCH_3 \longrightarrow CH_4 + \cdot CH_2OOCN{=}NCOOCH_3 \quad (8)$$

because no methane is detected.

Rate constants (based on nitrogen evolution) were measured for reaction 5 at 162°. The results of five repeat determinations yielded a value $k_5 = (6.4 \pm 0.9) \times 10^{-6}$ sec^{-1}, the error limit representing the average deviation of these runs. If a preexponential factor of 10^{14} sec^{-1} is assumed, this rate corresponds to an activation energy for reaction 5 of about 38 kcal mol^{-1}. This may be compared with a value of 34.6 kcal mol^{-1} for the activation energy reported[10] for the decomposition of tetramethyltetrazene, *i.e.*, where R is $(CH_3)_2N$· in reaction 1.

Decomposition in Dodecane Solution. When 10^{-2} *M* solutions in dodecane were decomposed thermally at temperatures in the range 120–170° or photochemically at a lower temperature, a colorless sticky polymerlike solid was produced which went brown on standing. The bright red solution was rapidly bleached, suggesting complete consumption of the azodiformate, although the maximum yield of nitrogen indicated that only about 7% of the azodiformate had decomposed.

Analysis of the polymerlike solid showed it to contain C, 44.1%; N, 12.6%; H, 6.4%; and O, 36.8% (by difference). This corresponds to a formula of $C_{17}H_{30}O_{11}N_4$, the molecular weight of which is 466, in reasonable agreement with the molecular weight of 500 ± 20 determined directly using a vapor pressure osmometer.

We consider that these results may be interpreted in terms of a ready addition of the radicals produced in reactions 5 and 6 to the azo linkage. The resulting radical then undergoes an isomerization reaction

$$CH_3OOC\dot{N}N(R)COOCH_3 \longrightarrow CH_3OC(\dot{O}){=}NN(R)COOCH_3$$

This radical in turn reacts by addition to the azodiformate and in this manner a repeating unit $(ON(COOCH_3)N{=}C(OCH_3)-)_n$ is built up. Our molecular weight determination suggests a value of about 3 or 4 for n. This ready addition reaction rapidly consumes all of the azodiformate and this explains why the solution is bleached, although actual thermal decomposition of dimethyl azodiformate based upon nitrogen evolution only accounts for a relatively small consumption of the ester.

It is clear that because of this complication the decomposition of azodiformate esters is not likely to be of use as a free-radical source.

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Intramolecular Elimination Reactions in the Photolysis of Fluoroaldehydes

Sir: Recently, perfluoroalkyl radicals have been generated by the photolysis of various fluoroaldehydes,[1] and data have been obtained for the abstraction of the aldehydic hydrogen atom by the radical

$$R_f + HCOR_f \xrightarrow{1} R_fH + COR_f$$

The aldehyde has also been used[2] as a radical source to investigate the removal of hydrogen from various substrate molecules, *i.e.*

$$R_f + RH \xrightarrow{2} R_fH + R$$

This technique is satisfactory if there is no other source of R_fH in the reaction system.

In a study of the photolysis of CF_3COCF_3–$HCOC_2F_5$ mixtures it became apparent that although the fluoroform formation could be adequately accounted for by the reactions

$$CF_3 + HCOC_2F_5 \xrightarrow{3} CF_3H + COC_2F_5$$

$$2CF_3 \xrightarrow{4} C_2F_6$$

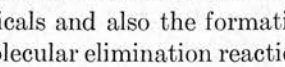
the pentafluoroethane formation was not similarly expressed by the reactions

$$C_2F_5 + HCOC_2F_5 \xrightarrow{5} C_2F_5H + COC_2F_5$$

$$2C_2F_5 \xrightarrow{6} C_4F_{10}$$

Our evidence for this conclusion was that although a plot of the ratio $R_{CF_3H}/R^{1/2}_{C_2F_6}$ *vs.* aldehyde concentration gave, within experimental error, zero intercept, a corresponding plot for $R_{C_2F_5H}/R^{1/2}_{C_4F_{10}}$ yielded a markedly positive intercept. Analysis of the data published for the $HCOC_2F_5$ system yielded essentially the same conclusion.

When cyclopropanecarboxaldehyde is photolyzed,[3,4] its decomposition has been shown to involve production of free radicals and also the formation of propylene by an intramolecular elimination reaction (8).



It seemed likely that such an intramolecular elimination reaction was also contributing to pentafluoroethane formation when the fluoroaldehyde was photolyzed; *i.e.*, the primary processes were

$$HCOC_2F_5 \xrightarrow{9} HCO + C_2F_5$$

$$\xrightarrow{10} CO + C_2F_5H$$

We have photolyzed under similar conditions the aldehyde alone and also aldehyde–nitric oxide mixtures. In the latter cases perfluorobutane formation was completely inhibited although extensive pentafluoroethane formation occurred, the yield decreasing by only ~75% at 400°K compared with the experiments performed in the absence of the inhibitor. We therefore conclude that reaction 10 contributes substantially to pentafluoroethane formation. The fact that only such a relatively small degree of C_2F_5H inhibition was observed, particularly with regard to the fact that, in the unscavenged experiments there will be substantial contributions to the C_2F_5 radical concentration by the decarbonylation of the COC_2F_5 radical produced in reaction 5, suggests that photodecomposition of the aldehyde by reactions 9 and 10 must be comparable.

Similar examination of the photolyses of $HCOCF_3$ and $HCOC_3F_7$ showed that the following intramolecular elimination reactions occur appreciably in these systems.

$$HCOCF_3 \longrightarrow CO + CF_3H$$

$$HCOC_3F_7 \longrightarrow CO + C_3F_7H$$

We therefore conclude that fluoroaldehydes are not suitable for use as photochemical sources of fluoroalkyl radicals in connection with hydrogen atom abstraction reactions and that the kinetic data reported[1,2] for such reactions are likely to be significantly in error.

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Reactions of Radicals Containing Fluorine

Part 4.—Reactions of Trifluoromethyl Radicals with Fluoroaldehydes

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The reactions of trifluoromethyl radicals, generated by the photolysis of hexafluoroacetone, with the aldehydes $HCOCF_3$, $HCOC_2F_5$ and $HCOC_3F_7$ have been studied and the following Arrhenius parameters determined:

	log A (mole^{-1} cm^3 sec^{-1})	E (kcal mole^{-1})
$CF_3+HCOCF_3 \rightarrow CF_3H+COCF_3$	11·95±0·10	8·8±0·2
$CF_3+HCOC_2F_5 \rightarrow CF_3H+COC_2F_5$	11·12±0·09	6·7±0·2
$CF_3+HCOC_3F_7 \rightarrow CF_3H+COC_3F_7$	11·09±0·11	6·6±0·2

The rate of hydrogen atom abstraction from the fluoroaldehydes at 164°C is independent of the size of the fluoroalkyl group. Direct photolysis of the aldehydes $HCOCF_3$, $HCOC_2F_5$ and $HCOC_3F_7$ is complicated by the intramolecular elimination reactions:

$$HCOR_f \xrightarrow{h\nu} R_fH+CO, \quad R_f = CF_3, C_2F_5 \text{ and } C_3F_7.$$

A value of 1·95, which is independent of temperature, has been obtained for the cross-combination af CF_3 and C_2F_5 radicals.

For a wide variety of aldehydes, the velocity constants for the hydrogen atom abstraction reactions (1) and (2) are similar and not influenced by the size of the alkyl group R.[1-3]

$$CH_3+HCOR \xrightarrow{1} CH_4+COR$$

$$R+HCOR \xrightarrow{2} RH+COR,$$

Replacement of the alkyl groups by fluoroalkyl groups, R_f, appears to have little effect on the rate of hydrogen atom abstraction when the attacking radical is methyl [4]:

$$CH_3+HCOR_f \xrightarrow{3} CH_4+COR_f.$$

The situation where the radical abstracting hydrogen from the fluoroaldehyde is a fluoroalkyl radical (reaction (4)) is less clear-cut and there appears to be a divergence between the results reported where R_f is CF_3 [5] and where R_f is C_2F_5 or C_3F_7, [6] the latter radicals being the more reactive in removing hydrogen atoms from the appropriate aldehyde:

$$R_f+HCOR_f \xrightarrow{4} R_fH+COR_f.$$

This difference might be real and ascribed to the nature of the attacking radical and the strength of the R_f—H bond formed, though D (CF_3—H) is stronger than in the other molecules,[7] or to the influence of the fluoroalkyl group on the reactivity of the aldehydic hydrogen atom. It might also reflect some complication in the photolysis of pentafluoropropionaldehyde or heptafluorobutyraldehyde leading to an additional source of R_fH in these decompositions.

A stndy of the reaction of the same fluoroalkyl radical with a variety of fluoroaldehydes should give information regarding some of these problems, and accordingly we have investigated the reaction of trifluoromethyl radicals with the aldehydes, CF_3CHO, C_2F_5CHO and C_3F_7CHO. Our data also enable the cross-combination ratio for CF_3 and C_2F_5 radicals to be evaluated and information to be deduced regarding hydrogen-atom abstraction from the parent aldehydes by the C_2F_5 and C_3F_7 radicals.

EXPERIMENTAL

APPARATUS AND PROCEDURE

The apparatus used has been described.[3] Trifluoromethyl radicals were generated by the photolysis of hexafluoroacetone at $\lambda > 3000$ Å. Because of the spectral overlap of the absorption bands of the ketone and the aldehydes used, there was also simultaneous photolysis of the aldehydes. Except for CF_3CHO, photodecomposition of the aldehyde does not influence the formation of CF_3H and C_2F_6. With CF_3CHO, the reaction was complicated by the formation of CF_3H by a direct intramolecular elimination reaction. We therefore used mixtures rich in ketone in order to obtain a relatively high CF_3 radical concentration so as to minimize the intramolecular contribution to CF_3H formation. Mixtures of aldehyde and ketone were made up in a 500 ml bulb before being expanded into the reaction cell. After reaction, the products were trapped at liquid-nitrogen temperature and the non-condensable gases removed by pumping. The remainder of the reaction products were then analyzed gas chromatographically, our technique permitting analysis of the compounds, CF_3H, C_2F_5H, C_2F_6, C_3F_7H, C_3F_8 and C_4F_{10}. Samples of C_2F_5H, C_3F_8 and C_4F_{10} were obtained by prolonged photolysis of the appropriate aldehyde or mixture of aldehydes and collecting the compounds as they were eluted from the gas chromatograph.

MATERIALS

Hexafluoroacetone was prepared by dehydration of the sesquihydrate (Koch-Light). The product contained small quantities of CO_2, C_2F_6 and CF_3H as impurities; these were removed by prolonged pumping at -130°C. The aldehydes were prepared from their hydrates as described previously.[4]

RESULTS AND DISCUSSION

REACTIONS OF CF_3 WITH $HCOR_f$

When trifluoromethyl radicals are produced in the presence of a fluoroaldehyde, fluoroform and hexafluoroethane are produced. Their formation may be accounted for by the reactions:

$$CF_3 + HCOR_f \xrightarrow{5} CF_3H + COR_f$$

$$2CF_3 \xrightarrow{6} C_2F_6.$$

Ayscough has measured the rate constant for the combination of trifluoromethyl radicals obtaining [9] the value k_6 (mole^{-1} cm^3 sec^{-1}) $= 10^{13.34}$. We use this value in the results discussed below.

$R_f = C_2F_5$

The reaction products analyzed for in this system were CF_3H, C_2F_5H, C_2F_6, C_3F_8 and C_4F_{10}. Our analytical data are shown in table 1. Their formation is discussed in terms of the following reactions:

$$CF_3 + HCOC_2F_5 \xrightarrow{7} CF_3H + COC_2F_5$$

$$COC_2F_5 \xrightarrow{8} CO + C_2F_5$$

TABLE 1.—HYDROGEN-ATOM ABSTRACTION FROM C_2F_5CHO BY CF_3 RADICALS

				rates of formation						
T°K	time (sec)	[ald]	[ket]	CF_3H	C_2F_6	C_2F_5H	C_3F_8	C_4F_{10}	$k_7/k_6^{\frac{1}{2}}$	ϕ
555·6	900	·250	·349	63·1	3·62	101	39·0	35·2	67·7	1·82
526·3	200	·522	·519	106	18·1	193	66·2	65·5	47·6	1·92
500·0	600	·300	·352	37·8	14·3	53·9	39·4	26·8	33·3	2·02
500·0	200	·500	·536	72·2	22·8	109	63·3	51·5	30·3	1·85
500·0	100	·111	·680	36·6	91·2	16·9	57·0	8·6	34·6	2·04
476·2	450	·287	·644	35·4	30·7	40·2	48·2	20·7	22·3	1·91
454·5	450	·688	·696	53·7	26·8	93·4	70·4	46·2	15·1	2·01
434·8	450	·399	·876	23·6	30·9	35·9	50·2	22·7	10·6	1·90
400·0	600	·676	·730	11·5	9·82	59·5	31·8	31·6	5·44	1·81
400·0	200	·157	2·36	9·98	79·4	11·6	46·7	7·2	7·13	1·95
400·0	600	·085	·587	3·78	52·1	5·3	28·0	4·2	6·17	1·90
400·0	200	·160	·989	8·53	90·4	11·6	51·5	7·1	5·61	2·04
400·0	600	·093	1·61	6·11	72·4	8·2	38·5	4·9	7·72	2·04
400·0	200	·459	1·40	17·6	26·7	37·8	48·4	20·8	7·45	2·06
400·0	450	·555	1·74	17·3	28·1	32·6	49·9	23·8	5·54	1·92
384·6	450	·724	·701	8·68	8·63	51·2	34·6	34·4	4·08	2·01
370·4	450	·553	1·18	8·21	22·8	31·9	49·3	26·1	3·11	2·03
357·1	450	1·19	1·13	5·41	4·47	60·0	25·8	41·1	2·15	1·91

ket = CF_3COCF_3; aldehyde and ketone concentrations in 10^6 mole cm^{-3}; rates of formation of products in 10^{12} mole cm^{-3} sec^{-1}; $\phi = R_{C_3F_8}/R_{C_2F_6}^{\frac{1}{2}}R_{C_4F_{10}}^{\frac{1}{2}}$.

$$C_2F_5 + HCOC_2F_5 \xrightarrow{9} C_2F_5H + COC_2F_5$$

$$CF_3 + C_2F_5 \xrightarrow{10} C_3F_8$$

$$2C_2F_5 \xrightarrow{11} C_4F_{10}$$

$$HCOC_2F_5 + h\nu \xrightarrow{12} HCO + C_2F_5$$

$$\xrightarrow{13} C_2F_5H + CO$$

$$CF_3 + HCO \xrightarrow{14} CF_3H + CO$$

$$C_2F_5 + HCO \xrightarrow{15} C_2F_5H + CO.$$

If reactions (7) and (9) are solely responsible for the formation of CF_3H and C_2F_5H respectively, then the following rate relationships apply:

$$R_{CF_3H}/R^{\frac{1}{2}}_{C_2F_6}[\text{ald}] = k_7/k_6^{\frac{1}{2}} \quad \text{and} \quad R_{C_2F_5H}/R^{\frac{1}{2}}_{C_4F_{10}}[\text{ald}] = k_9/k_{11}^{\frac{1}{2}}.$$

where R_X is the rate of formation of X and [ald] refers to the mean aldehyde concentration.

When $R_{CF_3H}/R^{\frac{1}{2}}_{C_2F_6}$ is plotted against the aldehyde concentration a linear plot is obtained which, within experimental error, passes through the origin. At 400°K e.g., the intercept for such a plot was $0{\cdot}17 \pm 0{\cdot}22 \times 10^{-6}$ and hence it may be concluded that there is no further source of CF_3H. Our data for reaction (7) are expressed by

$$\log k_7 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 11{\cdot}12 \pm 0{\cdot}09 - (6700 \pm 200)/2{\cdot}303\, \boldsymbol{RT}.$$

The error limits quoted in this paper are the standard deviations obtained by a least-mean-squares computer treatment.

C_2F_5 radicals are generated in this system by direct photolysis of the aldehyde and also by decarbonylation of the perfluoroacyl radical produced in the hydrogen-atom abstraction reactions. These radicals react by hydrogen atom removal from the aldehyde and also by auto-combination yielding C_2F_5H and C_4F_{10} respectively. A plot of the ratio $R_{C_2F_5H}/R^{\frac{1}{2}}_{C_4F_{10}}$ against aldehyde concentration reveals a markedly positive intercept, a value of $2{\cdot}4 \pm 0{\cdot}6 \times 10^{-6}$ (mole$^{\frac{1}{2}}$ cm$^{-\frac{3}{2}}$ sec$^{-\frac{1}{2}}$) being obtained for the experiments at 400°K. When the data of Pritchard *et al.*[6] for the experiments performed at 300°K are plotted in this manner, the dependence of their rate ratio on aldehyde concentration is small, a large intercept ($\sim 8 \times 10^{-6}$ mole$^{\frac{1}{2}}$ cm$^{-\frac{3}{2}}$ sec$^{-\frac{1}{2}}$) being obtained.

These observations suggest that there is a further contribution to the pentafluoroethane formation which probably involves photodecomposition of the aldehyde. Formyl radicals are produced by photolysis of the aldehyde (reaction (12)) and hence the disproportionation reaction (15) may contribute to C_2F_5H formation. We regard this reaction as unlikely since if it occurred then it would probably be paralleled by the cross-disproportionation of CF_3 and HCO radicals (14). Our zero-intercept for the aldehyde dependence of the ratio $R_{CF_3H}/R^{\frac{1}{2}}_{C_2F_6}$ indicates that no such reaction is occurring. We therefore conclude that (15) does not contribute to C_2F_5H formation in our experiments.

The intramolecular elimination of propylene in the photolysis of cyclopropanecarboxaldehyde has been established.[10] It seemed possible that photolysis of the pentafluoropropionaldehyde also involved an intramolecular elimination reaction such as (13) producing pentafluoroethane. To examine this possibility, we photolyzed

the aldehyde alone and also in the presence of sufficient nitric oxide to scavenge free radicals. We found complete inhibition of perfluorobutane formation but extensive formation of pentafluoroethane in the experiments with added nitric oxide. In similar experiments at 400°K, the rate of formation of C_2F_5H was reduced from 75×10^{-12} to 25×10^{-12} (mole cm^{-3} sec^{-1}) by the addition of nitric oxide. These observations suggest that there is extensive formation of C_2F_5H by reaction (13) and indicate that the Arrhenius parameters deduced by Pritchard *et al.*[6] are likely to be significantly in error.

We are therefore unable to calculate a value for k_9 from our data. A value may be estimated, however, by correcting for the intramolecular contribution to C_2F_5H (obtained from the inhibited experiments) and then calculating $k_9/k_{11}^{\frac{1}{2}}$ in the usual manner. By this means we have estimated a value of $8{\cdot}6\pm2{\cdot}8$ (mole$^{-\frac{1}{2}}$ cm$^{+\frac{3}{2}}$ sec$^{-\frac{1}{2}}$) for the rate constant ratio at 400°K. The corresponding value for $k_7/k_6^{\frac{1}{2}}$ is $6{\cdot}0\pm1{\cdot}1$, from which we may tentatively conclude that reactions (7) and (9) take place at very similar rates.

$R_f = C_3F_7$

The condensable reaction products observed in this reaction were CF_3H, C_2F_6, C_3F_7H and C_4F_{10}, but only the first two were consistently analyzed for. The reactions involved are:

$$CF_3 + HCOC_3F_7 \xrightarrow{16} CF_3H + COC_3F_7$$

$$COC_3F_7 \xrightarrow{17} CO + C_3F_7$$

$$C_3F_7 + HCOC_3F_7 \xrightarrow{18} C_3F_7H + COC_3F_7$$

$$CF_3 + C_3F_7 \xrightarrow{19} C_4F_{10}$$

$$HCOC_3F_7 + h\nu \xrightarrow{20} HCO + C_3F_7$$

$$\xrightarrow{21} C_3F_7H + CO.$$

The rate relation,

$$R_{CF_3H}/R_{C_2F_6}^{\frac{1}{2}}[\text{ald}] = k_{16}/k_6^{\frac{1}{2}},$$

may be obtained. The ratio $R_{CF_3H}/R_{C_2F_6}^{\frac{1}{2}}$ shows a linear dependence on aldehyde concentration the line passing through the origin within our experimental error, so that reaction (16) is the sole source of CF_3H formation. Our data are shown in table 2 and the velocity constant for (16) may be expressed by the equation:

$$\log k_{16}\,(\text{mole}^{-1}\,\text{cm}^3\,\text{sec}^{-1}) = 11{\cdot}09\pm0{\cdot}11-(6570\pm220)/2{\cdot}303\,RT.$$

In view of the intramolecular reaction established above for pentafluoropropionaldehyde, the photolysis of the heptafluoroaldehyde in the presence of nitric oxide was investigated. Considerable formation of heptafluoropropane in the inhibited system indicated that it was probable that reaction (21) was occurring. Accordingly, to study its formation by reaction (18) alone was not feasible in this work. The participation of reaction (21) in the direct photolysis of the aldehyde suggests that the reported [6] Arrhenius parameters for this reaction are incorrect.

$R_f = CF_3$

When the ketone and aldehyde are photolyzed together, CF_3H and C_2F_6 are produced as reaction products. The results reported above for photolysis of

$HCOC_2F_5$ and $HCOC_3F_7$ suggested that an intramolecular reaction leading to fluoroform formation might also occur for $HCOCF_3$. Accordingly, we photolyzed the aldehyde alone and in the presence of nitric oxide and found that, although C_2F_6 formation was eliminated in the inhibited experiments, substantial yields of CF_3H were obtained, indicating the occurrence of the reaction,

$$HCOCF_3 + h\nu \xrightarrow{22} CF_3H + CO.$$

We have attempted to reduce the contribution of reaction (22) to CF_3H formation in this reaction system by using mixtures rich in ketone. Accordingly we attribute the major contribution to the fluoroform formation to be reaction (23):

$$CF_3 + HCOCF_3 \xrightarrow{23} CF_3H + COCF_3$$

$$COCF_3 \xrightarrow{24} CO + CF_3.$$

The rate relation is

$$R_{CF_3H}/R^{\frac{1}{2}}_{C_2F_6}[\text{ald}] = k_{23}/k^{\frac{1}{2}}_6.$$

TABLE 2.—HYDROGEN-ATOM ABSTRACTION FROM C_3F_7CHO BY CF_3 RADICALS

T°K	t (sec)	[ald]	[ket]	rates of formation		$k_{16}/k_6^{\frac{1}{2}}$
				CF_3H	C_2F_6	
555·6	200	·500	·991	162	30·4	60·8
555·6	200	·326	1·20	136	37·3	71·5
526·3	200	·463	·918	126	25·5	55·2
526·3	200	·170	2·11	97·0	148	49·9
476·2	200	·269	3·33	92·1	245	22·7
434·8	300	·593	2·19	70·1	103	11·9
400·0	900	·915	1·81	36·2	41·6	6·25
400·0	100	·737	1·46	31·9	43·1	6·61
400·0	450	·391	1·44	19·7	73·4	5·96
400·0	900	·890	·859	23·4	12·2	7·61
400·0	150	1·44	1·39	37·6	11·7	7·66

ket = CF_3COCF_3; aldehyde and ketone concentrations in 10^6 mole cm^{-3}; rates of formation of products in 10^{12} mole cm^{-3} sec^{-1}.

Our results are shown in table 3. When the aldehyde was photolyzed alone a plot of the ratio $R_{CF_3H}/R_{C_2F_6}$ against aldehyde concentration showed a marked positive intercept ($\sim 20 \times 10^{-6}$ $mole^{\frac{1}{2}}$ $cm^{-\frac{3}{2}}$ $sec^{-\frac{1}{2}}$). When the results for the mixed system are plotted, the intercept is close to zero (1×10^{-6}) suggesting that most of the fluoroform formation is accounted for by reaction (23). We have used these data to calculate the velocity constant k_{23}:

$$\log k_{23}\ (\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = 11{\cdot}96 \pm 0{\cdot}10 - (8780 \pm 220)/2{\cdot}303\ \boldsymbol{RT}.$$

We have not included the results for experiments carried out at 400 and 416·7°K in our least-squares calculation since these data indicated curvature of the Arrhenius plot in this temperature region, presumably because at such temperatures contributions from reaction (22) to the total fluoroform yield are significant.

Our data are in reasonable accord with those obtained from a direct photolysis of the aldehyde by Dodd and Smith [5] who report $\log A_{23} = 11{\cdot}73$ and $E_{23} = 8{\cdot}4$ kcal $mole^{-1}$, and who also observed curvature of the Arrhenius plot below 425°K.

COMPARISON OF RATE CONSTANTS

In table 4 we have compared the kinetic data available for reactions of types (1), (3) and (4). From the results of the present work, variation of the fluoroalkyl group has little effect on reactivity of the aldehydic hydrogen atom since the rate constants for reactions (7), (16) and (23) are almost identical at 164°C, a conclusion which is in accord with results reported [1, 4] for reactions (1) and (3). The Arrhenius

TABLE 3.—HYDROGEN-ATOM ABSTRACTION FROM CF_3CHO BY CF_3 RADICALS

				rates of formation		
T°K	t (sec)	[ald]	[ket]	CF_3H	C_2F_6	$k_{23}/k_6^{\frac{1}{2}}$
555·6	100	·339	1·67	332	255	64·4
555·6	25	·235	1·16	258	217	75·4
555·6	100	·162	1·64	187	267	75·1
526·3	200	·119	1·27	66·4	193	42·3
526·3	100	·516	2·54	351	290	41·3
500·0	200	·183	1·96	72·5	266	25 3
476·2	200	·174	1·86	47·6	254	17·6
476·2	200	·321	1·58	85·8	225	18·3
454·5	200	·168	1·79	29·3	242	11·4
434·8	200	·162	1·73	21·0	250	8·3
434·8	300	·308	1·52	32·7	220	7·3
416·7	200	·144	1·53	14·0	228	6·5
416·7	200	·310	3·15	45·0	346	7·9
400·0	450	5·14	0·00	206	60·0	5·2
400·0	300	·246	1·54	14·4	112	5·6
400·0	100	·413	2·59	30·3	213	5·1
400·0	200	·328	1·61	21·5	222	4·4
400·0	450	·250	2·54	24·9	289	6·0

ket = CF_3COCF_3; aldehyde and ketone in 10^6 mole cm^{-3}; CF_3H and C_2F_6 in 10^{12} mole cm^{-3} sec^{-1}.

TABLE 4.—ARRHENIUS PARAMETERS AND VELOCITY CONSTANTS AT 164°C FOR HYDROGEN ATOM ABSTRACTION REACTIONS

reaction	log A (mole^{-1} cm^3 sec^{-1})	E (kcal mole^{-1})	log k (164°C) (mole^{-1} cm^3 sec^{-1})	ref.
CF_3+CF_3CHO	12·0	8·8	7·6	this work
$CF_3+C_2F_5CHO$	11·1	6·7	7·8	this work
$CF_3+C_3F_7CHO$	11·1	6·6	7·8	this work
CH_3+CF_3CHO	12·1	8·7	7·8	4
$CH_3+C_2F_5CHO$	12·9	9·8	8·0	4
$CH_3+C_3F_7CHO$	13·2	10·3	8·0	4
CH_3+CH_3CHO	11·9	7·6	8·1	1
$CH_3+C_2H_5CHO$	12·0	7·5	8·2	2
$CH_3+C_3F_7CHO$	11·8	7·3	8·1	1
CH_3O+CH_3OCHO	12·2	8·2	8·1	11

parameters for reactions (7) and (16) are similar but for trifluoroacetaldehyde the values are much higher, the difference being quite outside our experimental error. This difference of about 2 kcal $mole^{-1}$ in the activation energy requirements is unexpected and inexplicable since the rate constants in this region do not differ. The reactivity of the aldehydic hydrogen atom is slightly lower for the fluoroaldehydes indicating that fluoroalkyl groups have a slight deactivating effect on the hydrogen atom attached to the adjacent carbon atom.

Our " corrected " value for the rate constant for reaction (9) suggests that, as for alkyl radicals, the rate for the reaction $R_f + HCOR_f \rightarrow R_fH + COR_f$ is likely to be similar to the analogous reaction involving CF_3 radicals:

$$X + HCOX \rightarrow XH + COX$$

In table 4 we have also included data for the reaction of methoxyl radicals with methyl formate,[11] i.e., where $X = OCH_3$. Although there is little similarity in the Arrhenius parameters for the three systems where $X = CH_3$, CH_3O and CF_3, the velocity constants are almost identical at 164°C. It would be of interest to obtain data for the reaction:

$$(CH_3)N + HCON(CH_3)_2 \rightarrow (CH_3)_2NH + CO(NH_3)_2,$$

i.e., where $X = N(CH_3)_2$, to see if a comparable velocity constant was obtained or whether the similarity noted above is due primarily to the similarity of the H—C bond strength in the systems where $X = CH_3$, CH_3O and CF_3.

CROSS-COMBINATION OF CF_3 AND C_2F_5 RADICALS

When hexafluoroacetone + pentafluoropropionaldehyde mixtures are photolyzed, CF_3 and C_2F_5 radicals are produced. These may react by auto- and cross-combination yielding C_2F_6, C_4F_{10} and C_3F_8. The following relation holds:

$$R_{C_3F_8}/R^{\frac{1}{2}}_{C_2F_6}R^{\frac{1}{2}}_{C_4F_{10}} = k_{10}/(k_6^{\frac{1}{2}}k_{11}^{\frac{1}{2}}).$$

This rate ratio is the cross-combination ratio ϕ, and Kerr and Trotman-Dickenson [1, 12] have shown that for many alkyl radicals it has the value of 2, expected on the basis of the simple collision theory. Our results for this ratio ϕ are shown in column 11, table 2. The ratio is independent of temperature, within experimental error, and has the mean value 1·95. Gordon [13] has reported a value of 2·08 for this ratio and, for CF_3 and C_3F_7 radicals, Pritchard *et al.*[14] have obtained a value of 1·77.

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PRELIMINARY COMMUNICATION

COMPARISON OF THE REACTIVITY OF TETRAMETHYLSILANE AND NEOPENTANE TOWARDS FREE RADICAL ATTACK

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Recently, Chaudhry and Gowenlock[1] have measured the Arrhenius parameters for the reaction of methyl radicals with a series of Group IV tetramethyls and concluded that the central atom affected the reactivity of the C–H bonds towards methyl radical attack.

We have studied the abstraction of hydrogen atoms from tetramethylsilane by methyl and trifluoromethyl radicals; comparison of our data with the analogous reactions for neopentane should yield information regarding (1) the effect of substitution of the central carbon atom by silicon upon the Arrhenius parameters for the reactions:

$$CH_3 + (CH_3)_4X \rightarrow CH_4 + (CH_3)_3XCH_2$$

$$CF_3 + (CH_3)_4X \rightarrow CF_3H + (CH_3)_3XCH_2$$

and (2) the effect of the polar radical upon the C–H bond reactivity in these compounds.

Below we summarise the Arrhenius parameters and velocity constants at 164° (where 2.303 RT is 2000) for the neopentane and tetramethylsilane systems.

Reaction	Log A (mole^{-1} · cm^3 · sec^{-1})	E (kcal · mole^{-1})	log k (164°) (mole^{-1} · cm^3 · sec^{-1})	ref.
CH_3+$(CH_3)_4$Si	11.5 ± 0.2	10.3 ± 0.4	6.35	this work
CH_3+$(CH_3)_4$C	11.3	10.0	6.3	2
CF_3+$(CH_3)_4$Si	12.0 ± 0.1	7.6 ± 0.2	8.2	this work
CF_3+$(CH_3)_4$C	11.8	7.6	8.0	3

It is apparent that, for attack by the same radical, the Arrhenius parameters and velocity constants are identical, within experimental error, for neopentane and tetramethylsilane. We therefore conclude that substitution of the central carbon atom by silicon has little effect upon the reactivity of the adjacent C–H bonds.

Comparison of the abstraction reactions of the methyl and trifluoromethyl radicals with the same substrate shows that the effect of the polar radical is to markedly increase the velocity constant, there being a pronounced lowering ($\sim$ 2.5 kcal · mole^{-1}) of the activation energy requirements in both cases; this is in accord with results reported previously for hydrocarbon systems by Pritchard[4].

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